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THE STOKES METHOD FOR THE DETERMINA-
TION OF PYRITE AND MARCASITE.

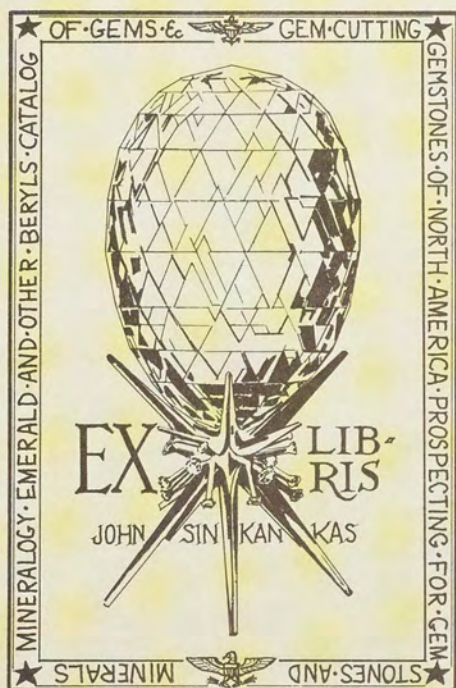
EFFECT OF TEMPERATURE AND ACIDITY IN
THE FORMATION OF MARCASITE (FeS_2)
AND WURTZITE (ZnS);
A CONTRIBUTION TO THE GENESIS OF
UNSTABLE FORMS.

By E. T. ALLEN and J. L. CRENSHAW.

MICROSCOPIC STUDY.

By H. E. MERWIN.





THE

AMERICAN JOURNAL OF SCIENCE

[FOURTH SERIES.]

ART. XXXII.—*The Stokes Method for the Determination of Pyrite and Marcasite*; by E. T. ALLEN and J. L. CRENSHAW.

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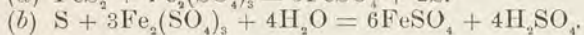
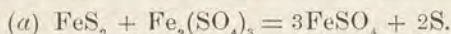
I. DEMAND FOR THE METHOD.

THE question whether a given specimen is pyrite or marcasite, in the case of well-crystallized natural material, will seldom arise; color and crystal form are generally sufficient criteria. For doubtful cases, which are more liable to be met with in synthetic products, few reliable tests exist, and for estimating either in mixtures with the other, the Stokes method is the only one known.

In a recent investigation by the authors, on the genetic conditions of certain allotropic forms, such a method became essential. We had already made some use of the Stokes method for identifying synthetic products, but had never carefully tested its accuracy. This has now been done; two serious sources of error have been detected and obviated, and some facts and relations of much more general interest have been discovered and worked out, in connection with it.

II. THE STOKES METHOD.*

The Stokes method depends on the difference in the behavior of the two minerals when boiled with a standard solution of ferric sulphate. The reaction takes place in two stages, thus:



Both minerals give the same products, viz., ferrous salt, sulphur and sulphuric acid; their difference is manifested in the relative *quantities* of the products, for experiment shows that about 52 per cent† of the sulphur in pyrite is oxidized to sulphuric acid, while only about 12 per cent of the sulphur in marcasite is oxidized. This behavior is not entirely unique. Penfield‡ found that concentrated nitric acid dissolved pyrite completely (i. e., all the sulphur is oxidized), while it leaves with marcasite a copious residue of sulphur. More recently, Arbeiter§ has made a long series of careful experiments with hydrogen peroxide and hydrochloric acid, in which he finds that marcasite always gives more free sulphur than pyrite under the same conditions. As the reagents are diluted the relation between the sulphur oxidized and the sulphur liberated approaches a simple constant ratio characteristic for each mineral. Arbeiter very plausibly infers that these phenomena are dependent on a difference in constitution between pyrite and marcasite.

To identify either pyrite or marcasite, Stokes determined the percentage of sulphur which was oxidized by a standard ferric sulphate solution. Before proceeding to show how the composition of a mixture of the two is determined, it will be best to explain the chemistry of the process in greater detail. The standard ferric alum solution, which contains close to 1 g.

* H. N. Stokes, Bull. U. S. Geol. Survey, 186.

† The numbers vary somewhat in different natural specimens. The numerical data here and in the sequel belong to a pyrite from Roxbury, Connecticut. Stokes' values were 60.5 and 16.5–18.0 for pyrite and marcasite respectively. These variations will be discussed farther on.

‡ Brush and Penfield, Determinative Mineralogy, 15th ed., p. 252.

§ Min. Chem. Untersuch. an Markasit, Pyrit und Magnetkies. Inaugural Dissertation, Breslau, 1913.

of iron and 5 g. free sulphuric acid per liter, is always used in the same quantity, 250°C in each experiment. The sulphide, finely ground and purified, is used in large *excess* (about 1 g.). The water of the solution is kept constant by a reflux condenser, while the influence of atmospheric oxygen is prevented by a stream of moist carbon dioxide which traverses the apparatus during the process. At the end of the test the ferric iron of the solution should be entirely reduced, partly by iron and partly by sulphur. A quantity of iron in the ferrous state which is constant for each mineral has passed into solution and a constant percentage of the sulphur has been oxidized. From the iron dissolved in our own experiments, we calculate that about 155 milligrams of marcasite are required in the reduction of 250°C of the standard solution, while only about 65 milligrams of pyrite are required for the same work. This of course is due to the fact that far less of the sulphur in marcasite is effective in reduction, nearly 90 per cent of it being precipitated in the free state. The complete data are given in the footnote.*

A. *Formula for the percentage of sulphur oxidized.*—Stokes determined directly the iron dissolved by the ferric salt, and calculated stoichiometrically the percentage of sulphur which was oxidized. Similarly, the percentage of sulphur oxidized in unknown *mixtures* of the two sulphides was estimated by him experimentally and a curve plotted which was used to determine their composition. The formula for the percentage of sulphur oxidized or the "oxidation coefficient" of either sulphide or of any mixture of the two was derived directly from equations *a* and *b*, viz. $(1) p = \frac{8.33b}{c-a} - 25$, where

* I. Pyrite. The increase of iron in solution after reduction with pyrite was equivalent to 4.46 g. KMnO_4 solution per 100°C , or for 250°C .

$2.5 \times 4.46 \times .001544$ (value of KMnO_4 solution) = KMnO_4	0.0172 g.
Equivalent to Fe	.0304 g.
Equivalent to FeS_2	.0652 g.
Total sulphur in .0652 g. FeS_2	.0348 g.
Fe reduced by Fe (see equation <i>a</i>)	.0608 g.
Fe reduced by S, $0.2500 - .0608$	.1892 g.
S reducing Fe, or S oxidized (see equation <i>b</i>)	.0181 g.
Percentage of S oxidized $\frac{.0181}{.0348}$	52.%

II. Marcasite. The increase of iron in solution after reduction with marcasite was equivalent to 10.57 g. KMnO_4 solution per 100°C .

Hence $2.5 \times 10.57 \times .001544 = \text{KMnO}_4$	0.0408 g.
Equivalent to Fe	.0721 g.
Equivalent to FeS_2	.1546 g.
Total sulphur in 0.1546 g. FeS_2	.0825 g.
Fe reduced by Fe (see equation <i>a</i>)	.1441 g.
Fe reduced by S, $0.2500 - .1441$	.1059 g.
S reducing Fe, or S oxidized (see equation <i>b</i>)	.0101 g.
Percentage of S oxidized $\frac{.0101}{.0825}$	12.3%

p = the percentage of sulphur in the decomposed sulphide which is converted into sulphuric acid; b is the ferrous iron at the end of the experiment originating both from the reduction of the ferric salt and from the decomposition of the iron disulphide; c is the total iron, ferrous and ferric,* at the end of the experiment; while a is the iron originally present in the standard solution. Our experiments soon showed that the reaction normally proceeds to the complete reduction of the ferric salt; b and c are therefore identical. Hence $p = \frac{8.33b}{b-a} - 25$,

or better written, since b is variable, (2) $p = \frac{8.33x}{x-a} - 25$.

B. *Relation of the iron dissolved to the composition of the mixture.*—A simpler relation than this and one more satisfactory in estimating the quantities of pyrite and marcasite in a mixture of the two is obtained by comparing directly x , the total quantity of iron in solution at the end of the test, with y , the percentage of pyrite in the sulphide mixture. Some results obtained by us before any such relation was suspected, indicated, when plotted in this way, a rectilinear relation; only the mixtures lowest in pyrite deviated much from a straight line (see fig. 1). Stokes concerned himself only with the relation between the composition of the sulphide mixture and the percentage of sulphur oxidized, but when his results are put into the same form they confirm our own. Table 1 gives the values of x , the total iron in solution at the end of the test, calculated by means of equation (2) from Stokes' published values of p . Our own value for a was used. a is the concentration in iron of the standard ferric solution. Both x and a are given in terms of a standard permanganate solution, 1 g. of which contained .001544 g. KMnO_4 ; and 100^{cc} of the ferric solution, measured at 25°, required 36.71 g. of this solution to oxidize it after reduction by sulphur dioxide. In fig. 2, Stokes' values for $(x - a)$, the iron dissolved by 100^{cc} of the standard ferric solution from pyrite-marcasite mixtures, are plotted against y , the percentage of pyrite which they contained. Here also the points fall into a nearly straight line, excepting those which stand for mixtures low in pyrite.

1. *Cause of the deviation of the values of x from a straight line.*—It seems decidedly probable that the low values for x in mixtures which contained 75%–100% marcasite were due to some disturbance in the reaction. This hypothesis would simply mean that the chemical action of the ferric solution on each sulphide in the mixture was proportional to its surface; that each sulphide acted independently of the other; and that the

* Stokes did not get a complete reduction of the standard ferric solution.

deviation in the line indicated that, in those mixtures where it occurred, the surfaces of the two minerals were no longer proportional to their weights. There was in fact some positive ground for this view, since it had already been noted by Stokes that marcasite was inclined to *flocculate* during the oxidation

FIG. 1.

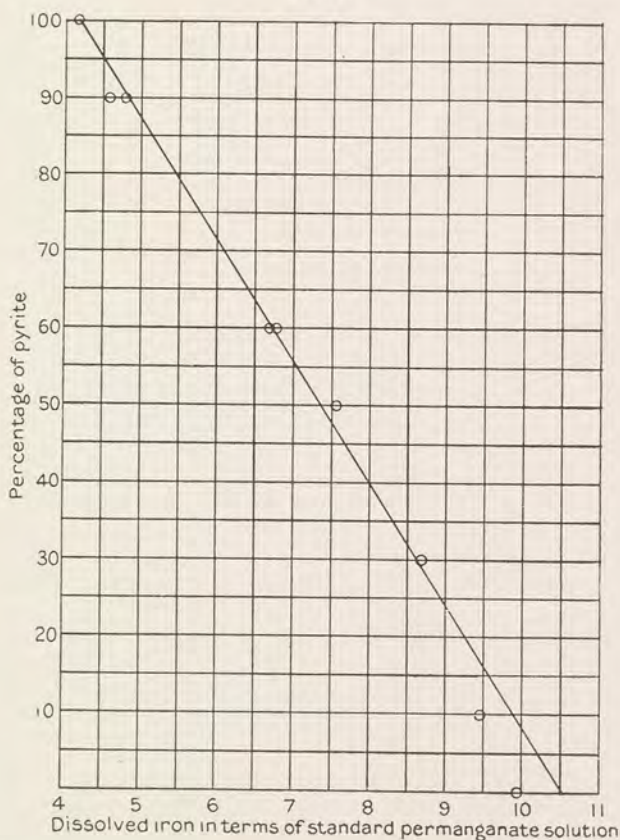


FIG. 1. Curve showing iron dissolved from pyrite-marcasite mixtures by a standard ferric solution. (Former results.)

tests. Flocculation would of course reduce the surface of the finely powdered marcasite, and if the pyrite were unaffected, the results would indicate too much pyrite, which as the reader may see, is exactly the direction of the errors in figs. 1 and 2. Many ways were tried to obviate the difficulty, but the only

TABLE I.

Stokes' values for x , the total iron in solution, and $(x-a)$, the iron dissolved from pyrite-marcasite mixtures by ferric sulphate solution.

Percent Pyrite	p = percentage of sulphur oxidized (experimentally determined)	x cal. from p by equation (2)	$(x - a)$ (the iron dissolved) $a = 36.71$
100	60.5	40.68	3.97
95	52.9	41.11	4.40
90	48.9	41.38	4.67
80	40.3	42.08	5.37
60	29.0	43.41	6.70
40	22.3	44.58	7.87
20	17.1	45.78	9.07
10	15.2	46.33	9.62
5	16.0	49.09	9.38
0	18.0	45.54	8.83

one which proved of any value was to shake the ferric solution and sulphide together with coarsely powdered quartz* and beads by means of which the lumps of sulphides were thoroughly ground up. Some details may make the operation clearer to the reader. The 500^{cc} boiling flask used in the oxidation experiments was fitted to a rubber stopper through which passed the reflux condenser (the cooling jacket of which was 20^{cm} in length) and a glass tube reaching to the bottom of the flask through which the carbon dioxide entered. 250^{cc} standard ferric alum solution with 2 g. quartz and about fifty beads of Jena glass were then added. The solution was now freed from air by boiling for ten minutes in the stream of carbon dioxide, and then cooled for fifteen minutes while the gas was still passing. Stokes' device for introducing the sulphide was used, viz., a small glass bucket suspended above the liquid by a platinum wire which passed up through the condenser. After the sulphide had been purified and dried for an hour in a vacuum desiccator, as shown farther on, it was quickly removed and poured into the bucket, the bucket attached to the platinum wire, and the flask again closed. The solution was now brought to boiling, while the bucket remained suspended above the liquid. Finally the bucket was dropped by drawing out the wire and the flask vigorously rotated for five or ten minutes, or until the powder seemed to fill the liquid and so remained, neither floating on the surface nor sinking to the bottom. The boiling was continued for two hours, when the ferric iron should be entirely reduced.

* This quartz contained only 0.04 per cent of oxides other than silica.

In some instances, for some unknown reason, the solution would fail to wet the sulphide satisfactorily, and the results would then be unsatisfactory.

(a) *Explanation of the low results with pure marcasite.*—The abnormal results for the sulphide mixtures low in pyrite

FIG. 2.

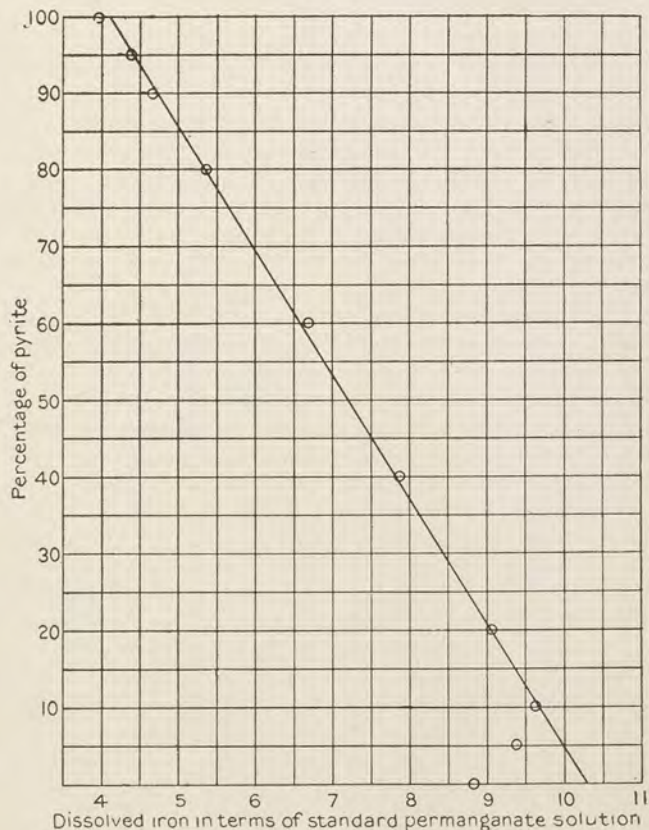


FIG. 2. Stokes' results on iron dissolved ($x-a$) from pyrite-marcasite mixtures by a standard ferric sulphate solution. The values for x are calculated from Stokes' published values for p , the percentage of sulphur oxidized.

are very well accounted for, as we have seen, on the supposition that the reactive surface of the marcasite is reduced by flocculation. In mixtures which contain 25 per cent or more of pyrite, flocculation rarely if ever occurs. Marcasite alone, however, gives somewhat too low results for the iron dissolved

($x-a$) unless it is shaken with quartz. Here, to be sure, there is no pyrite to compete with the marcasite in the reduction of the ferric salt, but it is not improbable that the sulphur which is set free might act as a competitor to the marcasite, so that less iron would dissolve in case the marcasite surface were diminished by flocculation. Stokes found, it is true, that ordinary powdered sulphur had scarcely any effect on the ferric solution and we have confirmed his results. From this it appears that such oxidation of the sulphur as normally occurs in the Stokes reaction is probably contemporaneous with the solution of the iron (see equations *a* and *b*, p. 372). Still the particles of separated sulphur are doubtless at first very small, and if the surface of the marcasite should become much reduced by flocculation, the slow reducing action of the sulphur might cease to be negligible. At any rate, our value for ($x-a$), the quantity of iron dissolved, was only 10.30 without quartz, and this value rose to 10.57 and 10.58 when quartz was used.

(b) *The necessary excess of the sulphide.*—We have found one other important source of error in the application of the Stokes' reaction which must be discussed before our final results are presented, viz., the quantity of sulphide which must be used. It will be recalled that 250^{cc} standard ferric solution is taken in each test, and that the quantity of the sulphide must be such as to reduce completely all the iron (250 mg.) present. If reproducible results are to be obtained, the excess of sulphide must be considerable. 0.75 g. gives virtually the same results as 1.0 g. for all mixtures containing 25 per cent of pyrite or more, but for other mixtures and for pure marcasite as much as 1 g. should be used. It will be noted on p. 373 that it takes much more marcasite than pyrite to reduce a given quantity of ferric iron. The ratio as determined by us is 2.37:1,* while Stokes found 2.26:1. The discussion of the relation between weight per cent and surface per cent given on p. 381 shows why the use of weights of the sulphides which are but little in excess of the quantity actually decomposed by the solution, would result in error, for in that case the *surface percentage*, which is the all important matter, would vary decidedly during the reaction, while in the ideal case it should be constant. It may be seen from the table (Table II) that the same results were obtained whether 1.5 g. or 1.0 g. marcasite was taken, and the same is also nearly true for pyrite. Stokes states that the fineness of the sulphide makes no appreciable difference in the results. We have never found any systematic

* This is the ratio between the constants for marcasite from Joplin, Mo., and pyrite from Roxbury, Conn.; the ratio for the *purest* natural minerals is about 2.5:1.

difference due to the time of grinding, though marcasite was repeatedly tested after grinding from 2 to 5½ h., pyrite from 1 to 2 h., and synthetic products from 1 to 2 h. It seems, therefore, to be true that after a sufficient excess of the sulphide is reached the results are unchanged by increasing the surface further, though more work would have to be done before this statement could be made unqualifiedly.

TABLE II.

Showing the relation between the composition of the sulphide mixture,* the iron dissolved, and the sulphur oxidized.

Per cent pyrite	(x - a) = iron dissolved			x	p = per cent of sulphur oxidized
	0.75 g. sulphide	1.0 g. sulphide	1.5 g. sulphide		
100	4.40	4.46	4.59	41.17	51.9
85	5.35	----	----	42.06	40.5
75	6.08	----	----	42.79	33.6
60	----	7.04	----	43.75	26.8
50	7.67	----	----	44.38	23.2
45	----	7.94	----	44.65	21.9
35	----	8.48	----	45.19	19.5
25	9.06	9.07	----	45.77	17.1
17	----	9.54	----	46.31	15.5
10	----	9.95	----	46.66	14.1
5	9.40	10.27	----	46.98	13.1
0	10.30	10.58	10.57	47.28	12.2

For all our work on either natural or synthetic products we have taken 1.05 to 1.1 g. and ground with water for 2 h. The sulphide is then removed from the mortar with a "policeman," filtered in a porcelain Gooch crucible on a hardened filter disc and kept in a vacuum desiccator till the next morning, when 1 g. of it is weighed out, boiled with dilute hydrochloric acid, poured on to a new hardened filter and finally washed, first with dilute hydrochloric acid and then with boiled water cooled in carbon dioxide. The washing is done in a special apparatus in which an atmosphere of carbon dioxide free from oxygen is maintained, for the details of which a former paper should be consulted.† *In these operations the total loss of material should be only a few centigrams.* If it is considerable

* The pyrite used was from Roxbury, Conn., and the marcasite was from Joplin, Mo.

† Allen, Crenshaw and Johnston, this Journal, (4), xxxiii, 169, 1912; Zs. anorg. Chem., lxi, 201, 1912.

from any cause, the results will be unsatisfactory for mixtures containing less than 25 per cent pyrite. Ignorance of this fact cost us much time in one stage of our work.

2. *Results on mixtures of the natural minerals.*—When the above precautions were carefully followed, we obtained the

FIG. 3.

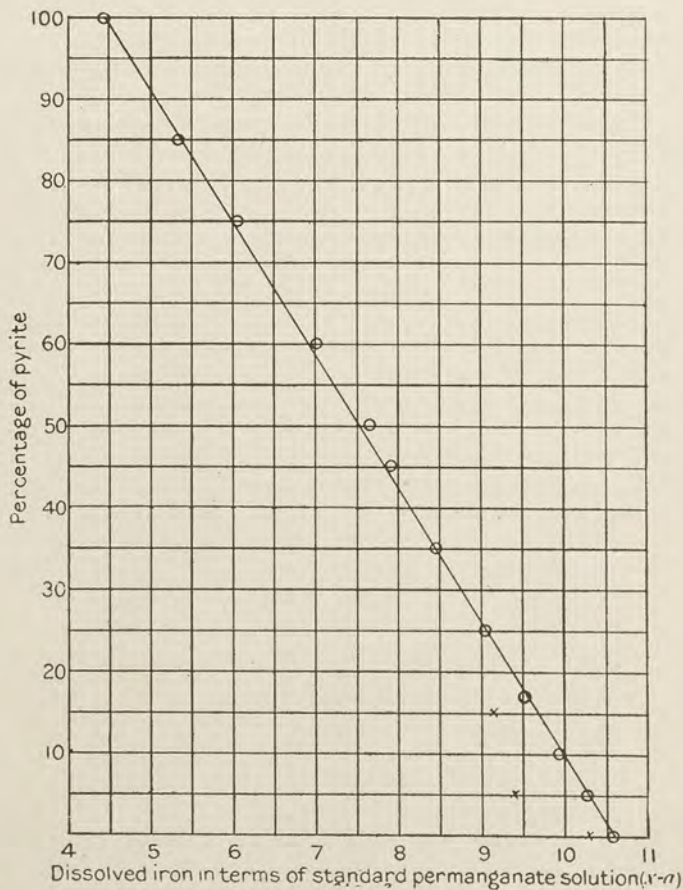


FIG. 3. Iron dissolved ($x - a$) from pyrite-marcasite mixtures by a standard ferric sulphate solution. Revised results. oo Results obtained by shaking with quartz. xx Results obtained without quartz. The pyrite was from Roxbury, Conn.; the marcasite from Joplin, Mo.

results given in Table II and graphically presented in fig. 3. It is evident that we have here a sensibly linear relation between the iron dissolved and the composition of the mixtures

reckoned in weight per cent, but before we consider in detail the meaning and accuracy of the results, it will be best to put the method on a safer footing by examining all other possible sources of error which we could discover.

3. Other sources of error in the Stokes method.

(a) *The ratio of the surfaces of the two minerals in weight percentage mixtures.*—In the first place if the active mass of each sulphide depends on its surface rather than its weight, as it should for solids, it will be obvious to the reader that the relation between $(x-a)$ the iron dissolved in the Stokes reaction, and y , the percentage of pyrite in the sulphide mixture, cannot be strictly linear in weight percentage mixtures, because the minerals naturally differ a little in density. They are of nearly the same hardness, and assuming that both are brought to the same degree of fineness when they are ground together, the percentage of surface of the marcasite, the lighter mineral, would be somewhat greater than its percentage by weight. Suppose that a mixture containing 50 per cent of each mineral by weight when ground in water,* consists of spherical particles of uniform size; then

$$\frac{n_1}{n_2} = \frac{S_m}{S_p} = \frac{5.03}{4.89}, \text{ where } n_1 = \text{the number of particles of mar-}$$

casite, n_2 = the number of particles of pyrite, and S_m and S_p the total surface of the two minerals respectively. The ground mixture of the minerals in equal quantities would therefore contain only 49.3 per cent instead of 50 per cent pyrite surface. This error, however, is approximately compensated, under the conditions described, by the more rapid action of the ferric solution on the marcasite particles. If all the particles are of the same size, those of each mineral must be uniformly attacked, and assuming the action of each is independent of the other, the *final surface of the marcasite* would be $s_m = n_1 4 \pi R_1^2$, and the *final surface of the pyrite* would be $s_p = n_2 4 \pi R_2^2$, where R_1 and R_2 are the radii of the particles of the two minerals at the end of the oxidation. It follows from the above that the final weights of the two minerals in a 50 per cent mixture where 1 g. was taken would be:

$$0.500 - \frac{0.155}{2} = 0.423 \text{ for the marcasite, and}$$

$$0.500 - \frac{0.065}{2} = 0.468 \text{ for the pyrite. (See also p. 373.)}$$

* To insure a more uniform size of grain as well as a more uniform mixture, each mineral was screened within similar limits before mixing, after which the mixture was ground in water.

Then $n_1 4.89 \frac{4}{3} \pi R_1^3 = 0.423$ and $n_2 5.03 \frac{4}{3} \pi R_2^3 = 0.468$.

$$\frac{n_1 4.89 \frac{4}{3} \pi R_1^3}{n_2 5.03 \frac{4}{3} \pi R_2^3} = \frac{.423}{.468} \therefore \frac{n_1 4 \pi R_1^2}{n_2 4 \pi R_2^2} = \frac{2.832}{2.946} = \frac{49.0}{51.0}$$

So while the pyrite in a 50 per cent mixture by weight would possess only about 49 per cent of the surface; *after the oxidation* by ferric sulphate, it would possess about 51 per cent. The average variation of the surface percentage from the weight percentage in the course of the reaction is therefore slight. By the same mode of reasoning we find that in a mixture of the sulphides containing 90 per cent by weight of marcasite, the surface of the latter would be 90.2 per cent before, and 89.7 per cent after the oxidation. Here also the average variation of the surface per cent from the weight per cent would be small. In a mixture containing 90 per cent by weight of pyrite, the pyrite surface would vary from 89.8 per cent to 91 per cent. Here the average variation of the surface from the weight per cent is also comparatively small, viz. 0.4 per cent.

The assumptions regarding the size, shape and uniformity of the particles are of course only approximations; still no other error has been found which could compensate any considerable error here and the conclusions deduced from the assumptions are in accord with the experimental results.

The plan naturally suggests itself, of taking the density of the two minerals into account in making the mixtures, and then increasing the quantity of the sulphide to be oxidized, so that the ratio of the surfaces of the two at the beginning should remain sensibly constant throughout the process of oxidation. Small quantities, however, are far more readily purified and otherwise handled, and it should also be noted respecting the application of the method to synthetic products that the latter are troublesome to prepare in quantity.

Although a careful study of other sources of error was made before the disturbance caused by flocculation was entirely understood, none of them proved of any great importance. It may be wise, however, to discuss them as briefly as possible.

(b) *Loss of water during the oxidation process.*—Stokes asserts that if the reaction flask is provided with a reflux condenser, and if the carbon dioxide which passes through the liquid during the process is first bubbled through water, there is no appreciable change in the concentration when a blank test is made with the standard solution. We can confirm this assertion as far as the water is concerned, but find a slight pre-

cipitation of iron even when 5 g. sulphuric acid instead of 4 g.* per liter is contained in the standard solution. If correction is made for the precipitated iron, no change in concentration has taken place, i. e., there is no loss of water. It should be stated that in an actual oxidation experiment no iron is precipitated, since the ferric iron is pretty rapidly reduced to the ferrous state. The following results prove these statements:

C_1 is the original concentration of the iron solution in grams of KMnO_4 solution per 100^{cc} of the standard.

C_2 is the concentration after the blank test, to determine which 100^{cc} solution is then reduced with SO_2 and titrated.

	I	II	III
C_1	37.06	37.06	36.54
C_2	{ 37.09	37.08	36.52
	{ 37.03	37.04	36.44

(c) *Reduction of the ferric solution during the blank test.*—Stokes states that no reduction occurred during a blank determination. We found a small reduction due perhaps to some organic matter associated with the ammonium salt. It amounted to only 0.1 g. of the very dilute standard KMnO_4 solution per 100^{cc}. In actual oxidations it is probable that the error would be less on account of the presence of a competing reducing agent.

(d) *Errors in the determination of the iron.*—These are very slight as previous results would indicate. In standardizing the ferric solution, 100^{cc} are measured in a calibrated flask at 25°. The solution is washed into a 500^{cc} flask, reduced in a stream of washed sulphur dioxide, the excess of which is boiled out in a stream of carbon dioxide in which the solution is finally cooled. The titration is then made with a weight burette, using a permanganate solution containing 1.5 g. of the salt per liter. The following determinations† of the concentration of four different solutions show the accuracy of the method:

I	II	III	IV
36.60	36.51	36.50	36.69
36.62	36.60	36.51	36.69
36.63	36.59	36.46	
	36.58	36.46	

Sulphur dioxide seems to carry with it mechanically some non-volatile reducing agent. This occasions a relatively large blank, but a very constant one. Blank tests were made as fol-

* The quantity prescribed by Stokes.

† The unit in these determinations is the gram of the above standard permanganate solution.

lows: A similar quantity of water to that used in the standardization tests was treated in the same way with sulphur dioxide and carbon dioxide successively. To the cooled solution was then added 0.86 g. ferric alum, thus giving practically the same conditions as those which obtain in the standardization itself. The quantity of the permanganate solution required in the blanks varied from 0.12 g. to 0.14 g. of permanganate solution, while 0.86 g. of ferric alum *alone*, with the usual amount of water, required always about 0.04 g. or one drop of permanganate solution. In the titration of an iron solution obtained in the Stokes process, the latter blank was subtracted, since here the ferric iron was reduced by the disulphide of iron and not by sulphur dioxide.

(b) *Oxidation of either ferrous solution or finely divided sulphide by atmospheric oxygen.*—The oxygen of the air, if not prevented, may affect the results in several particulars. First, when the finely ground sulphide is transferred from the desiccator to the reaction flask. This operation requires only about two minutes. The oxidation of 1–2 mg. of the sulphide would have an appreciable effect, but oxidation during this operation must be negligible, for a moist mixture of sulphides of similar weight to that used in the oxidation experiments exposed in a Gooch crucible to the air for 20 minutes gave an extract with distilled water which reduced only 0.1 g. permanganate solution.

The purification of the sulphide itself has been sufficiently insisted on by Stokes. He boiled it with hydrochloric acid, washed it successively with hydrochloric acid and boiled water cooled in carbon dioxide, in an atmosphere of carbon dioxide gas, and finally dried it in a vacuum desiccator. The apparatus which we employed in the washing has been described in a previous paper.* Whether necessary or not, we have dried the product more carefully than Stokes did. The washed sulphide in the Gooch crucible was removed from the above mentioned apparatus and put directly into a vacuum desiccator previously filled with carbon dioxide. The desiccator was then evacuated by a May-Nelson pump connected with driers which contained lime and phosphorus pentoxide. Thus any air in the desiccator was practically all removed in a couple of minutes. The sulphide was dried for about one hour, during which time the pump was kept running. It would seem impossible that any oxidation could have occurred during this process.

It may be said further that we assured ourselves by direct experiment with a titrated ferrous solution that no oxidation occurs when it is filtered in the described way. It has been

* Allen, Crenshaw and Johnston, loc. cit.

stated more than once by Baskerville and Stevenson* and others that an acid ferrous solution is not readily oxidized by the oxygen of the air, but we have here in addition the possibility of an oxidation of the finely ground sulphide. Since, however, moist sulphide oxidizes so very slowly even when exposed to the direct influence of the air, oxidation should be negligible when the filtration is done in our apparatus.

4. *Accuracy of the method.*—The systematic study of this problem has revealed only two considerable sources of error and means for obviating them have been explained. The results in fig. 3 involve errors of one per cent to two per cent. While this is a large error in ordinary analytical operations, it must be borne in mind that the two minerals are very similar and the method is very delicate. The total difference between the quantities of iron which the two minerals yield to the standard solution is, in terms of a dilute permanganate solution, only 6.1 to 6.4 g., according to the sample of pyrite taken, i. e., only 0.06 g. for every per cent. This amounts to about 1.5 drops of the permanganate solution, containing about 0.1 mg. of KMnO_4 and equivalent to only about 0.2 mg. of iron dissolved.

While the results are very constant for the same specimens of pyrite and marcasite, different natural specimens may show considerable differences.

Table III gives the results in tabular form. The only marcasites not of questionable purity which we have ever had in our hands, gave results which were almost identical. The results on the Joplin marcasite also served to show the constancy of the method; the first two results were obtained about a year later than the third with different standard solutions. The two determinations on Elba pyrite No. 1 were also made a year apart. The determinations for synthetic pyrite were made on two different preparations.

The variations on different occurrences of the same mineral species are due in part, if not entirely, to impurities. Thus the Leadville pyrite contains copper probably as chalcopyrite which Stokes found to give low results. Elba pyrite No. 1 is the purest we have ever found; the quantity at our disposal was unfortunately insufficient for this investigation. Elba pyrite No. 2 contained a little cobalt, but hardly sufficient to cause the irregularity noticed. It was selected from a large sample which contained considerable hematite, traces of which were probably retained by the sulphide even after purification. That the suspicion was well founded was proved by the fact that after the ground mineral had been treated for two days at 200° with two per cent sulphuric acid saturated with hydrogen

* J. Am. Chem. Soc., xxxiii, 1104, 1911.

TABLE III.

Showing the Stokes Constant for Different Pyrites and Marcasites.

Mineral.	Locality.	$x - a$	Impurities.
Pyrite	Leadville, Col.	3.95	0.1 per cent of copper.
"	Elba, No. 1	4.17 4.20	none found except .04 per cent quartz.
"	Elba, No. 2	4.35	0.04 nickel and cobalt—mostly the latter, ferric oxide suspected.
"	" " after heating with sulphuric acid at 200°	4.18	
"	Roxbury, Conn.	4.46	1.4 per cent arsenic.
"	Synthetic, prepared by heating synthetic marcasite	4.14 4.11	
Marcasite	Joplin, Mo.	10.57 10.58 10.52	only quartz found
"	Galena, Ill.	10.57	
"	* Synthetic at 25°	10.20 10.34	may contain pyrite
	" " 200°	10.27 10.42	" " "
	" " 300°	10.20 10.34	" " "

* See this Journal, The effect of temperature and acidity in the formation of marcasite and wurtzite, (4), xxviii, 411, 1914.

sulphide, the value of the Stokes constant agreed with the purest pyrite. The hematite had evidently been removed by the treatment. The Roxbury pyrite which was used for the most part in the present work was selected on its macroscopic appearance, the higher results being at first regarded as more accurate. Later, when the lower results with synthetic pyrite had thrown them under suspicion, an analysis showed the presence of arsenic. Stokes found that arsenopyrite gave high results; 1 per cent arsenic in that form having the same effect in the Stokes test as 2 per cent marcasite, while it may be seen from the table that 1.4 per cent arsenic in the Roxbury pyrite has the same influence as 4 per cent marcasite.

5. *Linear relation between any pyrite and any marcasite.*—It is important to note in this connection that the constants of any pyrite and marcasite are additive in their mixtures. Thus a number of tests showed this to be true of the Elba pyrite No. 2 and the Joplin marcasite, while more numerous experiments (see fig 4) show the same thing for the Joplin marcasite and Elba pyrite No. 1. This is a fact of importance in the appli-

cation of the method to synthetic mixtures, which has been the object of the present investigation.

(a) *Independence of the chemical action of the two sulphides.*—Since the quantity of iron which dissolves in the Stokes reaction is approximately a linear function of the composition of the sulphide mixtures, each sulphide in the mixture behaves

FIG. 4.

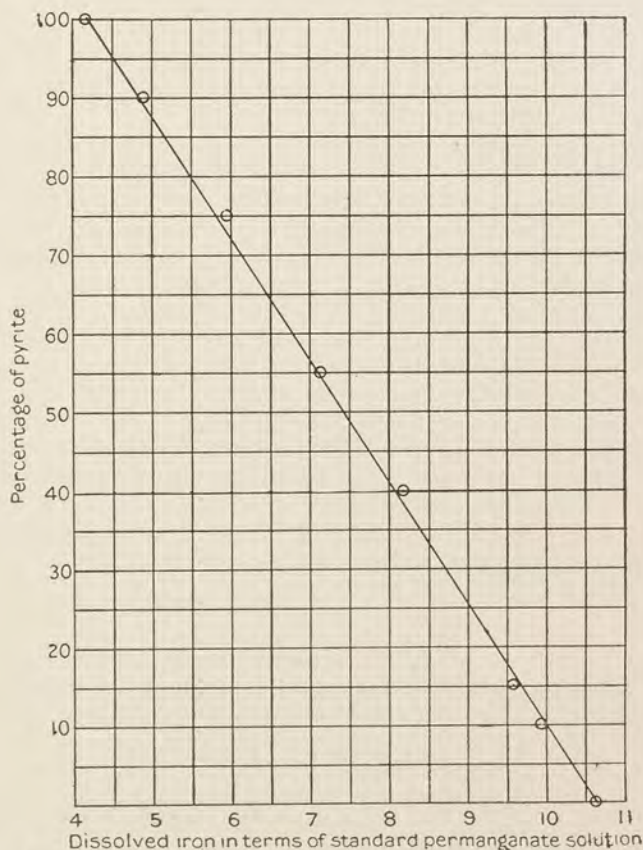


FIG. 4. Iron dissolved from pyrite-marcasite mixtures by a standard ferric solution. Pyrite from Elba; marcasite from Joplin, Mo.

with the solution practically as it does when alone. The iron which dissolves comes only from decomposed sulphide, consequently in a sulphide mixture the quantity of each decomposed is directly proportional to its percentage in the mixture. Thus in a 50 per cent mixture, one half as much of each mineral is decomposed as when each reacts alone with the solution.

Further, each sulphide in the mixture must reduce only its proportional fraction of the solution; in a 50 per cent mixture the pyrite must reduce one half of the ferric solution and the two sulphides must reduce the two portions at the same rate,—otherwise the one which worked faster would encroach on the province of the other and the results would not be linearly related. In other words, the results are the same as if one should first separate the two minerals, divide the solution between them in proportion to their percentages, and allow each constituent to reduce its own portion separately.

The rate at which the solution is reduced by the two sulphides must then be the same for each mineral, but the rate at which each mineral is decomposed is quite different; *that* is proportional to the quantity of iron ($x-a$) which each yields to the solution. This quantity, in terms of the standard permanganate solution, is 4.20 for pyrite (Elba No. 1) and 10.57 for marcasite. *Marcasite is therefore decomposed 2.5 times as rapidly as pyrite, while the solution is reduced at the same rate by each.*

(b) *Electrolytic effect in the Stokes reaction.*—From the findings of Gottschalk and Buehler,* and of R. C. Wells,† one would expect an electrolytic effect here. If there is one, it must be very small. The results in fig. 3 do indeed appear to form a slightly convex curve which means of course that the marcasite seems to have a little more than its proportionate effect. Possibly this may be attributed to electrolytic influence.

(c) *Stokes' curve.*—If the relation between x and y is linear, $x = by + c$. By substituting in this equation the values x_0 and x_{100} for x , when $y = 0$ and $y = 100$ respectively, i. e., when we have pure marcasite and pure pyrite, we obtain

$$(3) \quad x = \frac{x_{100} - x_0}{100} y + x_0.$$

Now substituting this value for x in equation (2) (page 374) the latter becomes

$$(4) \quad y = \frac{(p + 25)a - (p + 16.66)x_0}{(p + 16.66) \left(\frac{x_{100} - x_0}{100} \right)}$$

or if we replace x_0 , x_{100} and a by their experimental values, viz., 47.28, 41.17 and 36.71, we have $y = \frac{10.57 p - 129.8}{.0611 p + 1.018}$. This curve, which is evidently a hyperbola, is plotted in fig. 5. The *plotted curve* is a true hyperbola *calculated* from the values which fall on the line drawn between the values of $(x-a)$ for pyrite and marcasite respectively; the *points plotted* are the values of p calculated directly from experimental values of x .

* Gottschalk and Buehler, *Econ. Geol.*, vii, 28, 1912.

† R. C. Wells, *ibid.*, vii, 571, 1913.

These are the figures for Roxbury pyrite and Joplin marcasite. We have seen above that these results are affected by the presence of arsenic in the Roxbury pyrite. In fig. 6 are graphically shown the Stokes constants ($x-a$), for the purest natural pyrite and marcasite (Curve 1, 1) and also for the synthetic minerals (Curve 2, 2). It must be admitted that the

FIG. 5.

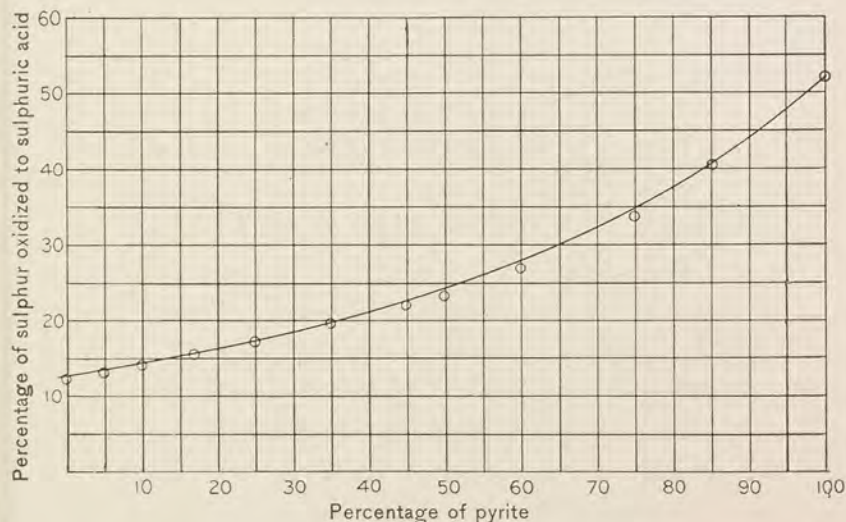


FIG. 5. Curve showing sulphur oxidized in pyrite-marcasite mixtures by a standard ferric solution. Roxbury pyrite. Joplin marcasite.

value 10.3 for synthetic marcasite is open to the suspicion that the products may have contained a little pyrite.* Fig. 7 shows the hyperbolas calculated from these results, the assumption being made that the constants are exactly additive in their mixtures, while the points plotted are, as in fig. 5, calculated from the experimental values as given in fig. 4.

Fig. 8 shows Stokes' published values for p plotted against y . The plotted curve is again a true hyperbola calculated from the values of x which fall on the line in fig. 1. The minimum in his curve which Stokes obtained at 10 per cent pyrite seems therefore to have no real existence.

Summary.

1. The Stokes method for determining pyrite and marcasite, alone or in mixtures, depends on the estimation of the

* This Journal (4), xxxviii, 411, 1914.

iron dissolved when the finely ground and purified sulphide is treated with a boiling standard solution of ferric alum. The same pyrite or marcasite gives very constant values and the influence of each in mixtures is additive, i. e., there exists a linear relation between the iron dissolved and the composition of the mixture. The sum of the errors usually amounts to

FIG. 6.

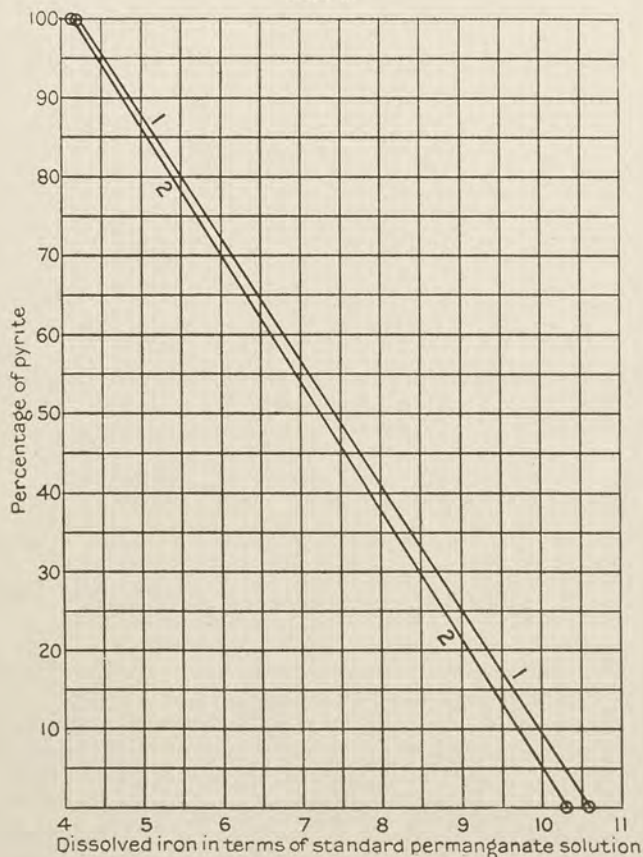


FIG. 6. 1, 1. Values of the Stokes' constant ($x-a$) for the purest natural pyrite and marcasite, and their mixtures.

2, 2. Values of the Stokes' constant for synthetic pyrite, synthetic marcasite and their mixtures.

about 1 per cent, reaching a maximum of 2 per cent. There are two important sources of error. First there must be a sufficient excess of the sulphide, which is many times greater

FIG. 7.

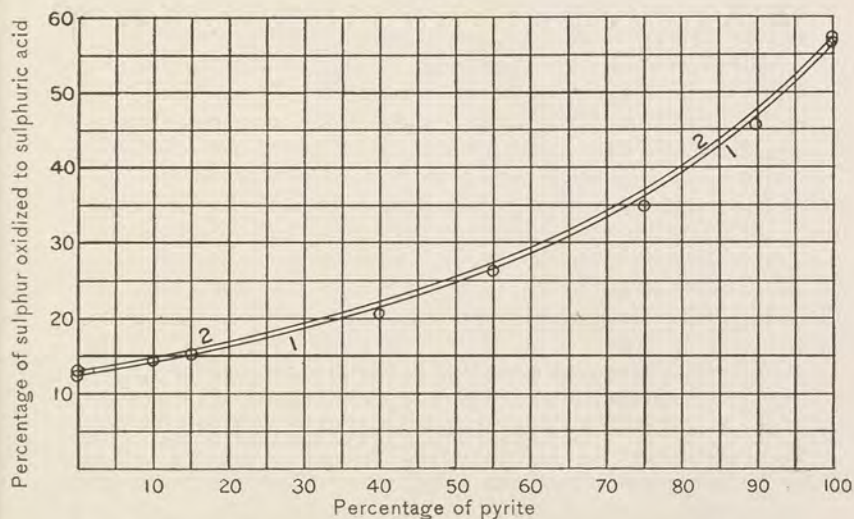


FIG. 7. Curves showing sulphur oxidized in pyrite-marcasite mixtures by a standard ferric solution. 1, 1. Curve for purest natural pyrite and marcasite. 2, 2. Curve for the synthetic minerals.

FIG. 8.

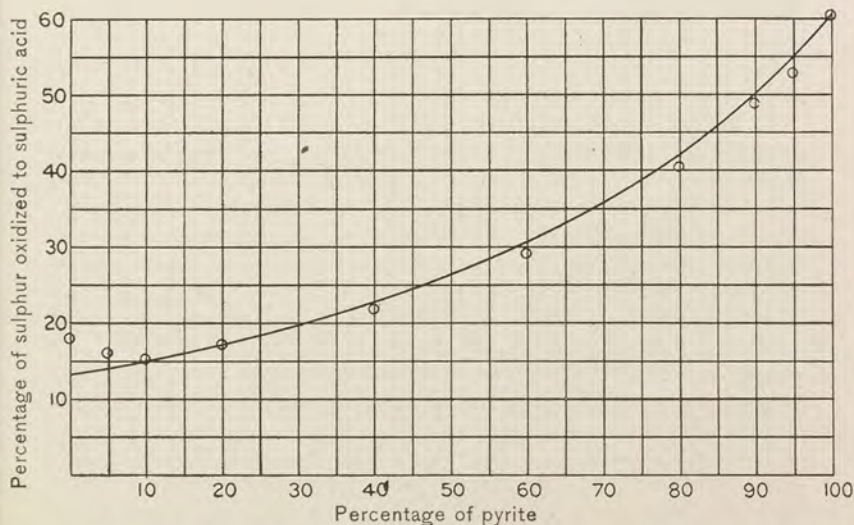


FIG. 8. Curve showing sulphur oxidized in pyrite-marcasite mixtures by a standard ferric solution. Stokes' results. The curve is a true hyperbola.

(7-15) than the amount required by theory. With such an excess the percentage of the surfaces remains on the average nearly the same as the percentage by weight, the basis on which the mixtures are made up. About 1 g. is sufficient for 250^{cc} of the standard solution. Secondly, the marcasite has a characteristic tendency to flocculate and thus reduce its reacting surface. This difficulty may be avoided by shaking the reaction mixture with pure quartz and beads until the lumps of the powder are thoroughly disintegrated. *Different specimens* of pyrite and marcasite give with the Stokes reaction values which differ somewhat. The differences are due in some cases, if not in all, to the presence of impurities. It is unfortunate that small quantities of impurities which will reduce ferric iron or give up iron to the solution exercise a serious influence. It is therefore not always possible to decide between a natural pyrite and a pyrite containing several per cent of marcasite by the Stokes reaction alone, nor to determine accurately the percentage of each in a natural mixture. In an investigation on the conditions of formation of pyrite and marcasite, this method has been very useful.

2. The results with the Stokes method plainly indicate that each mineral behaves in a mixture of the two just as it does alone; each appears to reduce a quantity of solution which is proportional to its surface; and each appears to reduce the solution at practically the same rate. The rates at which the sulphides are decomposed is quite different for the two minerals, because more of marcasite than of pyrite is required to reduce a given quantity of ferric iron. The ratio of these rates is not far from 1:2.5.

3. That ferric sulphate dissolves from pyrite a smaller quantity of iron than it does from marcasite means simply that more reduction is effected by sulphur in the case of pyrite, in other words that more of the sulphur in pyrite is oxidized. Stokes considered only the relation of p , the percentage of sulphur oxidized, to y , the percentage of pyrite in the sulphide mixture. We have shown that this curve is a hyperbola. This characteristic behavior of pyrite and marcasite towards oxidizing agents is probably general. It has been found by other observers that nitric acid and hydrogen peroxide both oxidize more of the sulphur in pyrite under the same conditions.

The authors wish to thank Prof. E. S. Dana of Yale University and Drs. Geo. P. Merrill and Edgar T. Wherry of the National Museum for specimens of pyrite and marcasite used in this work.

Geophysical Laboratory,
Carnegie Institution of Washington.

ART. XXXIII.—*Effect of Temperature and Acidity in the Formation of Marcasite (FeS_2) and Wurtzite (ZnS); A Contribution to the Genesis of Unstable Forms*; by E. T. ALLEN and J. L. CRENSHAW. *Microscopic Study*; by H. E. MERWIN.

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I. INTRODUCTION.—DETERMINATIVE INFLUENCE OF ALKALINITY AND ACIDITY ON CRYSTALLINE FORM.

IN the course of an investigation of the disulphides of iron, it was found by the authors that the stable form, pyrite,* is the only crystalline form which is obtained by the action of alkali polysulphides on ferrous salts. The first product of this reaction at room temperature is a mixture of amorphous ferrous sulphide and sulphur, from which the disulphide gradually forms. The formation is very slow at low temperatures, and, even at 100°, the product appears to be at first amorphous, but it crystallizes in time to pyrite with excess of reagent—a transformation which could not be effected with natural marcasite under similar conditions. From *acid* ferrous solutions, on the other hand, by the action of sulphur and hydrogen sulphide the unstable form marcasite is obtained. The marcasite is commonly admixed with pyrite, the quantity of which may be reduced by raising the initial concentration of the free acid; or increased by raising the temperature.

The same regularity was observed to hold good for the sulphides of zinc and mercury,† i. e. only the *stable* forms, sphalerite and cinnabar, were obtained from alkaline solutions; while only from *acid* solutions could the corresponding unstable forms, wurtzite and metacinnabar, be obtained. This peculiar regularity seemed to us of sufficient interest to form the subject of a separate investigation. There has never been any doubt about the products of the alkaline solutions, but a more thorough study of the products of the acid solutions seemed desirable, more especially as so little is known about the genesis of unstable forms. We have been obliged to confine ourselves to the investigation of marcasite and wurtzite, for, while our synthetic black sulphide of mercury is an unstable crystalline form and conforms to the above rule in crystallizing from acid solutions, it could not be absolutely identified with the natural metacinnabar, and its formation has thus far been brought about only within a very limited range of conditions.

II. MARCASITE AND PYRITE.

A. *Preparation*.—The marcasite-pyrite mixtures were prepared by heating in sealed tubes, a 5 per cent solution of hydrous ferrous sulphate,‡ containing a measured quantity of sulphuric acid, sulphur and hydrogen sulphide. A Jena glass tube of about 17–18^{mm} internal diameter and closed at one end

* This Journal, xxxiii, 169, 1912; Zs. anorg. Chem., lxxii, 201, 1912.

† This Journal, xxxiv, 341, 1912; Zs. anorg. Chem., lxxix, 125, 1912.

‡ In one series of experiments ferrous chloride and hydrochloric acid were taken.

was first constricted at a point about 50^{cm} from the closed end, to a diameter of 6 or 8 millimeters. The ferrous sulphate and sulphur were then dropped in through a long funnel; a sufficient quantity of a titrated sulphuric acid (30 per cent con.) was measured out from a burette into a graduated cylinder, enough water added to make 75^{cc} and the resulting solution poured into the tube. The tube was then packed in ice, saturated with hydrogen sulphide and quickly sealed at the constriction, after which it was placed in a steel bomb surrounded by water and closed up. The bomb was finally put into a suitable furnace already heated to a degree such as to bring the bomb to the desired maximum temperature. For details of bomb and furnace construction a former paper* should be consulted. At the end of a period of from 1-4 days, depending on the temperature of the experiment, the bomb was withdrawn from the furnace, cooled and opened, and the tube then removed. The glass tube should never be so long that it cannot be entirely covered by water; partially covered tubes are very apt to break.

B. *Purification of the synthetic products.*—The glass tube is opened and the contents quantitatively transferred to a suitable beaker. The sulphide is then filtered out while the filtrate is caught in a measuring flask of 250^{cc} capacity and, after adding the washings, diluted up to the mark.

In the solution the acid is determined by titrating with a standard sodium carbonate solution using methyl orange as indicator. The excess of hydrogen sulphide, or of sulphur dioxide, which forms when the temperature and acidity are sufficiently high, should first be removed by boiling in a current of carbon dioxide. The sulphide needs to be carefully freed from sulphur in all cases, and it was thought best to get rid of the siliceous matter originating from the glass when the products were formed at the highest temperatures. To this end the wet sulphide is first dried by washing with alcohol and ether and sucking off with the pump. Most of the sulphur is then dissolved out by carbon bisulphide, but the film which commonly persists and coats the sulphide as the last portions of the volatile solvent evaporate, should be removed by concentrated colorless ammonium sulphide, after the excess of carbon disulphide has been washed out by ether. The excess of ammonium sulphide is then removed by water and the product finally dried with alcohol and ether; or if siliceous material is present the product should be warmed with a mixture of hydrofluoric and hydrochloric acids for half an hour on the steam-bath. The sulphides should be kept in a vacuum desiccator. When they are to be tested by the Stokes reaction

* Loc. cit.

1.05 to 1.1 g. is ground for 1 h. with water in a McKenna ore-grinder and further purified as described in the preceding paper.*

Disulphide of iron was formed by the above method at 25°, 100°, 200° and 300°. All the products with the possible exception of those obtained at 100° were evidently crystalline to the naked eye, and those obtained at the higher temperatures, especially the products formed from solutions which contained 2 per cent to 3 per cent of sulphuric acid consisted of crystals of relatively large size. The finest were crystallized from hydrochloric acid solutions; these formed beautiful aggregates of splendid lustre the individuals of which were not infrequently 0.7^{mm} in length $\times$ 0.2–0.3^{mm} in width.

C. Chemistry of the formation of iron disulphide.—The chemical reaction which is involved in the formation of iron disulphide is expressed by the equation:

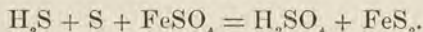


Table I may be put in evidence on this point. The figures there given show that the increase in acidity and the weight of the sulphide formed are in practically the ratio which the equation demands. This is strictly true within the limits of error at the lower temperatures, 25° and 100°. To be sure the errors are greater than they are in ordinary gravimetric operations because we are under the necessity of recovering the sulphide in pure condition; what clings to the filter can not be saved by burning and this fact entails an appreciable loss.

At the higher temperature and the higher acid concentrations a side reaction becomes manifest, viz: the reduction of the sulphuric acid to sulphur by the hydrogen sulphide, followed in turn by the interaction of the sulphur with the sulphuric acid and the appearance of sulphur dioxide. This reaction is pretty slow at 200°. The first series of results at this temperature (see Table I) show very little reduction; the second series more. The cause of this difference is not clear. At first it was ascribed to differences in the glass tubes, which were taken from two different lots. The glass of the second lot was believed to have neutralized more acid than the other. Blank experiments made by heating dilute sulphuric acid in sealed tubes at 200° show that the suspicion was incorrect, but the results are given because the behavior of "Jena combustion" glass with aqueous solutions at 200° is a matter of some interest (see Table II). At 300° the reduction of sulphuric acid by hydrogen sulphide and sulphur is considerably greater in the same time than it is at 200° (see Table I).

* This number, p. 384.

Thus after one day's heating sulphur dioxide is formed if the initial acid concentration reaches 1 per cent, and it appears after a longer time where the acid is weaker. *At no temperature, however, do these side reactions appear to have any connection with the crystalline form of the product.*

TABLE I.

The relation between the sulphide formed and the acid set free.

Temperature	FeS ₂ found	Gain in wt. of acid calc. from FeS ₂	Gain in wt. of acid found	Final acid in wt. % calc.	Final acid in wt. % found	Initial acid in wt. %
25°	2.46	2.01	2.23	0.115	0.127	0.015
"	3.67	3.00	3.18	.165	.173	.015
"	4.31	3.52	3.51	.235	.234	.059
100°	1.32	1.08	1.11	1.54	1.58	0.10
"	.93	.76	.73	1.26	1.22	.25
"	.68	.55	.55	1.23	1.20	.50
"	.43	.35	.37	1.47	1.50	1.00
"	1.03	.84	.86	2.62	2.65	1.50
200°	0.71	0.58	0.60	1.27	1.30	0.50
"	.96	.78	.74	2.04	2.00	1.00
"	.96	.78	.75	2.54	2.49	1.50
"	.93	.76	.70	3.01	2.90	2.50
"	.68	.55	.52	3.24	3.19	2.50
200°	1.02	0.83	0.68	2.10	1.91	1.00
"	.82	.67	.49	2.14	1.90	1.25
"	.81	.66	.47	2.64	2.37	1.75
"	.74	.61	.34	2.81	2.45	2.00
"	.73	.60	.33	3.30	2.94	2.50
300°	1.18	0.95	0.74	1.36	1.08	0.10
"	1.04	.85	.61	2.13	1.82	1.00
"	.81	.66	.30	2.89	2.40	2.00
"	.29	.24	.17	3.32	2.78	3.00

TABLE II.

Neutralization of H₂SO₄ by Jena combustion glass at 200°*

Time = 3 days.

Grams H ₂ SO ₄ taken	Grams H ₂ SO ₄ found after heating	Grams H ₂ SO ₄ neutralized	Concentration H ₂ SO ₄ in wt. % before heating	Concentration H ₂ SO ₄ in wt. % after heating
0.1937	0.1859	0.0078	0.97%	0.93%
0.3874	0.3752	0.0122	1.94	1.88
0.2949	0.2875	0.0074	2.95	2.88

* The surface exposed to the action of the acid was about 30 cm².

D. *Analysis of the products.*—The molecular ratio between the two products of the interaction of hydrogen sulphide, sulphur and a ferrous salt is strong evidence of the composition of the precipitate. This had already been directly proved by chemical analysis to be the disulphide,* while the color, luster and chemical behavior agreed with pyrite or marcasite. The purposes of the present investigation necessitated a method for determining whether we had one or the other, or both. In the preceding paper† we have shown how the Stokes method may be utilized for this purpose. The method is founded on the difference in the chemical behavior of the two crystalline forms toward oxidizing agents. A boiling standard solution of ferric alum dissolves a characteristic and constant quantity of iron from each of the minerals pyrite and marcasite, and these constants are additive for mixtures of the two; i. e., the quantity of iron dissolved by ferric alum is a linear function of the composition of the mixture. We may anticipate the results so far as to say that the Stokes method indicates in all cases, with the possible exception of the products formed at 100°, that the sulphides are either pure marcasite or mixtures of marcasite and pyrite.

E. *Other evidence on the nature of the products.*—Certain objections to exclusive reliance on the Stokes method will occur to the chemist. The products are all crystallized from solutions containing an excess of ferrous salt as well as hydrogen sulphide. Sulphur dioxide also is a final product in many instances. Any of these impurities if occluded by the precipitate would disturb the Stokes test; the ferrous salt by directly increasing the iron in solution; the sulphur dioxide or hydrogen sulphide by reducing the standard solution and thus decreasing the iron which should normally dissolve.

Many instances are known of occlusions which are impossible to remove by ordinary washing. But the purification of these sulphides was out of the ordinary in that the substance was *ground in a mortar for two hours* before boiling with hydrochloric acid and washing with water. Such drastic treatment might be expected to remove these occlusions if any are present. Still we have positive evidence that the products which we infer to be mixtures of pyrite and marcasite from the Stokes tests are really such, rather than marcasite containing reducing impurities.

1. *Microscopic evidence.*—The identification of opaque minerals as compared with the transparent minerals is much less fully worked out. In default of optical constants, one must rely on crystal form, color, cleavage and on microchem-

* This Journal (4), xxxiii, 173, 1912; Zs. anorg. Chem., lxvi, 206, 1912.

† This number, p. 371.

ical tests where they are available. Synthetic sulphides, prepared as above described, except where hydrochloric acid is used, consist of crystals which are usually not sufficiently developed to make microscopic diagnosis certain. Apart from any other evidence, color and crystal habit in most of the preparations make the presence of marcasite almost certain, but that of pyrite doubtful. When the preparations are made in *double tubes* (see p. 412), however, the crystals are well developed, and Larsen* found pyrite in many of them; the marcasite was always better developed, in fact, the crystals were often measurable, though some crystals of pyrite were 0.5^{mm} across. The pyrite crystals usually showed a combination of the cube and octahedron.

2. *Color*.—Pyrite is distinctly yellower than marcasite, though in making comparisons care should be taken that the specimens are untarnished. Synthetic products which consist of very small crystals can not be satisfactorily compared for color differences by simply placing small portions side by side; but by grinding a few tenths of a gram to a rather fine powder and then boiling in a small beaker with dilute hydrochloric acid (to remove tarnish), a considerable amount can be made to float on the surface of the liquid in the form of a metallic mirror. When examined in this way, the products which were determined by the Stokes reaction to be either pure marcasite, or very near it, showed the same color as a mirror of the natural marcasite obtained in the same manner, while products found by the Stokes reaction to contain 28 per cent and 35 per cent pyrite respectively, formed mirrors of decidedly yellower color, identical with that of pyrite-marcasite mixtures, as three observers all agreed. This test, while purely qualitative, gave evidence which may be regarded of considerable weight.

3. *Evidence concerning inclusions*.—It has already been admitted that the synthetic sulphides might possibly have occluded ferrous sulphate, hydrogen sulphide, or in some cases sulphur dioxide, and that any of these substances would interfere with the Stokes test and the conclusions drawn from its use. The absence of hydrogen sulphide was pretty conclusively shown by a series of experiments in which the synthetic sulphides were heated in *vacuo*. These experiments were made on products formed at 200° under conditions where sulphur dioxide never formed.

A vertical glass tube about 1^{cm} in diameter, closed at the lower end, was used for heating the sulphide. About 15^{cm} from the lower end a side tube 5^{mm} in diameter was sealed on. Above the side tube the vertical tube was constricted and left

* This Journal (4), xxxiii, 215, 1912; Zs. anorg. Chem., lxvi, 251, 1912.

open at the top. The side tube was sealed direct to one arm of a U-tube of the same diameter (5^{mm}) stuffed with glass wool. The U-tube was about 18^{cm} high and during the experiments was surrounded by ice to condense any free sulphur. The other arm of the U-tube was sealed to the absorption tube. This was about 1^{cm} in diameter drawn down to 5^{mm} at either end and contained a layer of pure solid caustic soda about 6^{cm} in length, which was kept in place by plugs of glass wool. The free end of the absorption tube was sealed to a May-Nelson vacuum pump. When the apparatus was made ready the sulphide was dropped through a small funnel into the vertical tube, which was then sealed off at the constriction.

The sulphide was heated by a small resistance furnace by which the vertical tube was surrounded. The apparatus was, of course, evacuated before the heating began and the pump was kept running during the experiment.* The temperature in all the experiments, where not otherwise stated, was carried to 600° measured by a thermoelement, the hot junction of which touched the glass on the outside of the tube close to the sulphide. The time required to reach this temperature was about three-quarters of an hour. The current was then turned off, for under these conditions considerable decomposition of the disulphide into pyrrhotite and sulphur always took place, thus leaving no reasonable room for doubt that all the gas was driven off.

After the heating was over, the furnace was removed and the tube quickly cooled, air was admitted to the apparatus, the absorption tube cut out, the soda dissolved in water and freed from glass wool by filtering. The solution was then tested with cadmium chloride and if yellow cadmium sulphide came down, a sufficient excess of the reagent was added, the precipitate filtered and washed, and finally dissolved in ammonia and perhydrol. The solution was then just acidified and precipitated hot with barium chloride. After the nature of the sulphur compound had been sufficiently well established the use of the cadmium salt was omitted and the soda solution directly oxidized by perhydrol.

The results are shown in Table III. All the synthetic sulphides gave off hydrogen sulphide when heated, but the facts plainly indicate that this was not present originally in the sulphide, but was formed by the action of water, during the heating, on the pyrrhotite, one of the decomposition products of the disulphide; † for when pure natural marcasite was ground

* None of the gas escapes by this method. In the last experiment in Table III, the apparatus was isolated from the pump by a stopcock after evacuation and before heating. The results were practically the same.

† When the maximum temperature was only 350°, much less pyrrhotite was formed and far less sulphur was obtained.

TABLE III.

Showing the hydrogen sulphide obtained by heating natural and synthetic iron disulphide to 600° in vacuo.

Sulphide tested 1 g. in all cases	Quantity of pyrite in the product determined by the Stokes test.	Quantity of H ₂ S obtained in terms of BaSO ₄	Quantity of H ₂ S calculated in milligrams
Joplin marcasite, ground in water	none	7.6 milligrams	1.1
Joplin marcasite, ground in water	none	8.1 “	1.2
Joplin marcasite, ground dry	none	0.0 “	0.0
†Joplin marcasite, heated in 2% H ₂ SO ₄ 2 days at 200°	30-40%	8.1 “	1.2
Synthetic FeS ₂ at 200° from 0.1% HS ₂ O ₄ , ground in water	45%	12.2 “	1.8
Synthetic FeS ₂ at 200° from 0.1% H ₂ SO ₄ , ground in water	45%	9.7 “	1.4
Synthetic FeS ₂ at 200° from 1% H ₂ SO ₄ , ground in water	28%	5.7 “	0.8
Synthetic FeS ₂ at 200° from 2% H ₂ SO ₄ , ground in water	3.5%	20.0 “	2.9
Synthetic FeS ₂ at 200° from 2.5% H ₂ SO ₄ , ground in water	26%	17.1 “	2.5
Synthetic FeS ₂ at 200° from 2.5% H ₂ SO ₄ , ground in water	26%	16.2 “	2.4

for 2 h. in water and purified like the synthetic products for the Stokes test, it gave off hydrogen sulphide on heating in vacuo; whereas the same mineral ground dry for 2 h. gave off none. It is also certain that the water could not have come

† Ground in water before heating.

from any other source than the moist sulphide itself; it could not have come from the soda, since pyrrhotite crystallized from a fusion and ground dry, gave off no hydrogen sulphide even when heated for an hour or more at 700° under similar conditions.

A careful study of the table (Table III) proves that the quantity of hydrogen sulphide given off by the products bears no relation whatever to the quantity of pyrite indicated by the Stokes test. Thus a preparation which, according to the Stokes test, contained 28 per cent pyrite, gave off less hydrogen sulphide than the natural marcasite; and the preparation which contained the least pyrite (3%–5%) gave off more hydrogen sulphide than the one which contained the most pyrite (45 per cent). True, the synthetic preparations usually gave off more gas than the natural mineral, but we attributed this difference to the greater fineness and hence larger surface of the former, a condition which is well known to favor the retention of water. That the synthetic products are finer-grained appears from the fact that they are more readily transformed into pyrite. Thus products which contained originally 5 per cent and 45 per cent pyrite, after heating in vacuo for about 1 h. at 300° to 350° showed 21 per cent and 62 per cent respectively, while pure natural marcasite after the same treatment had changed only to the extent of 6 per cent. Previous experience in this laboratory shows that fine powders are transformed into polymorphic modifications more readily than coarse materials.

Though no direct experiments for the detection of any possible sulphur dioxide or ferrous sulphate in the synthetic sulphides were made, there was no indication of the presence of either. Only the products formed at a maximum temperature of 300° could have contained sulphur dioxide, because none was formed under other conditions. If we accept the conclusion that at 200° the products occluded no reducing impurities, there is no reason to believe that occlusion occurred at 300° . The composition of the three-hundred-degree products as determined by the Stokes reaction shows a similar dependence on the acid concentration as that of the two-hundred-degree products; both curves are smooth and the relation between them is rational (see fig. 1).

In regard to the occlusion of ferrous sulphate in the products, we can simply say that its presence would increase the quantity of iron dissolved in the Stokes reaction, which would then indicate too much marcasite, while, on the contrary, in the products obtained at three different temperatures (25° , 200° and 300°) the maximum percentage of marcasite indicated was always the same—not far from 100 per cent as com-

pared with Joplin marcasite—never more than 100 per cent as would be expected if ferrous salt was occluded.

Thus, while it would be difficult, if not impossible, to prove that the synthetic products contained no inclusions, everything indicates that they do contain pyrite, and that the quantity of it is regularly influenced by increasing acid concentration and by temperature, as we shall see farther on.

4. *Analogous behavior of zinc salts.*—Further light is thrown on the nature of the synthetic iron disulphides by the

FIG. 1.

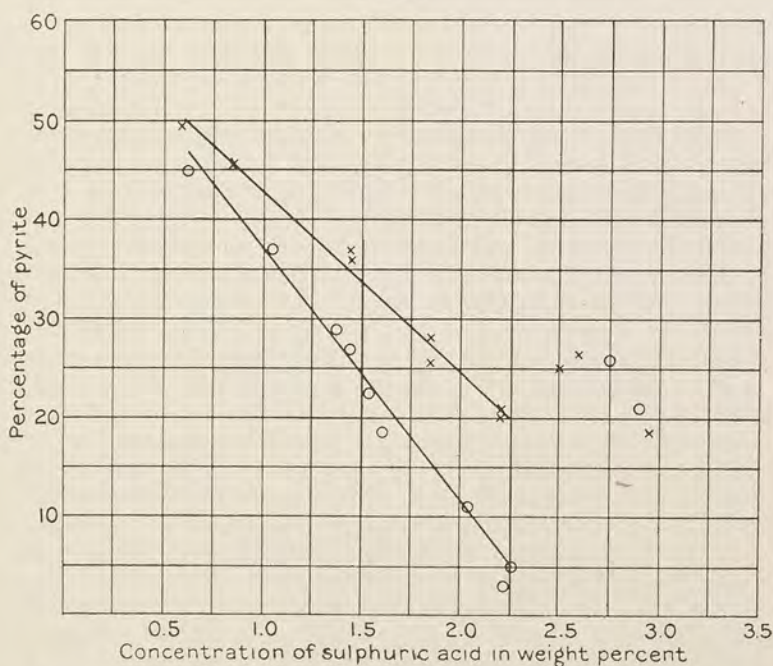


FIG. 1. The effect of acid concentration on the formation of iron disulphide.

o = 200° ; x = 300°

similar behavior of the zinc sulphides. We shall find in the next chapter that acid exerts the same specific influence on the sulphide of zinc that it does on the disulphide of iron, i. e., it causes that substance to crystallize in an unstable crystalline form—wurtzite. But there also the unstable form is commonly mixed with the stable form sphalerite. Now the method employed to identify the zinc sulphides is entirely different from that used for the iron sulphides. Because of

the transparency of the former, optical tests are the most practical. Yet we arrive at the same general conclusion in both cases: viz, that the product of hydrogen sulphide on acid solutions very commonly gives *both* crystalline forms.

F. *Effect of temperature and acidity on the crystalline form of the products.*—The two variables of prime importance in their effect on the crystalline form of iron disulphide are temperature and acid concentration. Experiments were made at several temperatures, as follows:

1. *The products at 25°.*—In bottles of about 2.5 liters capacity were put a 5 per cent solution of hydrous ferrous sulphate, several grams of powdered sulphur and a variable quantity of sulphuric acid. The bottles were packed in ice and their contents saturated with hydrogen sulphide. Several series of these bottles were tightly stoppered and left to stand at room temperature for periods of many months. Excepting a single instance no precipitate was ever obtained where the initial concentration was as high as 0.03 per cent by weight of sulphuric acid even when the time was lengthened to a year. Precipitation always resulted when the initial acid was as low as 0.015 per cent.* As Table I shows, precipitation started in one instance where the initial acid was 0.059 per cent. This bottle had been used before for the same purpose, so that one might suspect some crystal nuclei had been left behind; yet in other cases crystals intentionally added had no effect when the original acid was .03 per cent. Whatever the cause, there can be no doubt of the fact, for the data in Table I show a close equivalency between the acid and the sulphide formed. This is not a solubility phenomenon, for again the table shows that the precipitation once started will proceed in a concentration far beyond the above figure.

A few data on the rate of formation may be of some interest. The first two experiments in the table required about one month, the third 80 days. The products in all cases were crystalline powders and microscopic examination indicated that crystallinity was complete.

The results of the Stokes method were in good accord. In Experiment 3 (Table I), where the final acid concentration was 0.23 per cent, the value obtained for $(x - a)$, the dissolved iron, was 10.20, corresponding to 94 per cent of marcasite. Where the final acid was 0.17 per cent, $(x - a)$ was 10.34, equivalent to 96 per cent of marcasite. These figures depend on results obtained with the purest natural marcasite we have yet found, but not all natural marcasites show exactly the same value for $(x - a)$, and farther on we shall give a reason for believing that this product is pure synthetic marcasite.

* Wrongly given 0.15 per cent in a previous paper, loc. cit.

Below the concentration 0.015 per cent H_2SO_4 , we have made no effort to experiment; we were deterred by the fear of getting amorphous products except possibly from solutions of very low iron concentration, and these on account of the small yield would be impractical to work with. Alkali sulphide solutions at this temperature unquestionably give pyrite, but what may happen in the narrow field between these two classes of solutions, i. e., in neutral or barely acid solutions, has not yet been experimentally proven. (For further considerations on the significance of these experiments for the formation of marcasite in nature, see pp. 427-429.)

2. *The products at 100°.*—The results obtained on the sulphides precipitated at 100° were unsatisfactory. Not only was no regular relation between the composition and conditions of formation of the products found, but the results were not reproducible. The products at all other temperatures gave results consistent with one another, and the peculiar behavior of these has not been fully explained. In general it was found that the products contained more marcasite for a given acidity than at higher temperatures, and the products all seemed to be preponderantly marcasite; apparently none contained more than 25 per cent pyrite. This was as it should be, but none of the products seemed to be pure synthetic marcasite, as we should expect from the results at other temperatures. Their anomalous behavior is possibly due to the presence of some amorphous disulphide. The products are for the most part crystalline; but most if not all contained a variable quantity of a fine, black powder which did not show any crystalline form or luster under the microscope. The occurrence of *amorphous zinc sulphide* of low refractive index was common in the zinc sulphides and if any amorphous material was present in the iron sulphides it would doubtless affect the results. One would expect, however, that the Stokes constant ($x - a$) would be higher for the amorphous substance than for marcasite, since it is higher for marcasite than pyrite, and the amorphous sulphide is less stable and more soluble than marcasite, as marcasite is less stable and therefore more soluble than pyrite. As a matter of fact, the constant ($x - a$) was always lower for these products than for marcasite. It may also be stated that the color of the films floated on water (p. 339) were somewhat different from those of marcasite-pyrite mixtures. Judging from the Stokes method, the products ranged from 15 per cent to 25 per cent pyrite.

3. *Products at 200° and 300°.*—Most of the investigation of the iron disulphides centers on the products formed at 200° and 300°. Probably because these were better crystallized, the results were always reproducible and the relations between

them were regular. Of course, ideal conditions of formation would include precipitation at constant temperature and constant acidity, but even though these can not as yet be completely controlled, we have been able to determine the direction and regularity of the influence of each factor on the crystal form of the product. To keep the acidity constant would be a well-nigh impossible task, for it will be borne in mind that the formation of every molecule of sulphide is necessarily accompanied by the generation of a molecule of acid, and to keep the volume so great that the acidity would remain sensibly constant while enough sulphide is obtained for experimental purposes would be practically out of the question.

(a) *Method of plotting.*—It is obvious that if the acid exerts a specific influence on the composition of the product, the latter should be changing from moment to moment so long as precipitation continues. Two different products formed from the same initial acid could only contain the same percentage of the two crystalline forms when the weight of each product was the same. If the latter varied by a chance variation in the quantity of hydrogen sulphide, or by a variation in the time of reaction, the composition of the sulphide would also change. The abscissa used in the figure is therefore the *average acidity* (fig. 1). The results are tabulated in Table IV.

(b) *Significance of the curves.*—The curves show clearly that the greater the acidity up to a certain point, the greater is the percentage of marcasite formed at either temperature; and the higher the temperature for a given acidity the greater is the percentage of pyrite formed.

The sensibility of the product to the influence of acid is extraordinary; even a difference of 0.1 per cent in the average acid concentration makes a difference of about 2.5 per cent of pyrite. The decrease in the acidity with falling temperature required in the formation of pure marcasite is also notable, and, when taken together with the results at the lowest temperature, 25°, this fact throws interesting light on the natural genesis of the mineral. The highest percentage of marcasite we have been able to get at 300° from sulphuric acid solution is about 80 per cent; at 200° the quantity increases to 95 per cent—the same percentage as was obtained at 25° and at 300° from hydrochloric acid solutions.

(c) *Irregularity at high acid concentrations.*—The plot shows further that when a product is formed in an acid of more than about 2.25 per cent average acidity, there is a sudden and somewhat irregular increase in the percentage of pyrite. We supposed at first that marcasite would be found to change when heated in acids of this concentration and higher, and experiment seemed to confirm this; for pure

TABLE IV.

Showing the percentage of pyrite obtained in synthetic products at observed temperatures and acid concentrations.

Temperature	Initial acid concentration in wt. %	Final acid concentration in wt. %	Average acid concentration in wt. %	(x-a) iron dissolved in the Stokes reaction	Percentage of pyrite
200°	0.10	1.14	0.62	7.77	45
	.75	1.35	1.05	8.23	37
	1.00	1.88	1.44	8.84	27
	1.00	1.73	1.38	8.75	29
	1.25	1.83	1.54	9.15	22.5
	1.50	1.78	1.64	9.41	18.5
	1.75	2.32	2.03	9.89	11
	2.00	2.50	2.25	10.27	5
	2.00	2.42	2.21	10.42	3
	2.50	3.00	2.75	8.94	26
	2.75	3.05	2.90	9.22	21
300°	0.10	1.08	0.59	7.43	49.5
	0.50	1.20	0.85	7.71	45.5
	1.00	1.90	1.45	8.26	37
	1.00	1.90	1.45	8.30	36
	1.50	2.22	1.86	8.97	25.5*
	1.50	2.20	1.85	8.78	28.0
	2.00	2.38	2.19	9.31	20.0
	2.00	2.40	2.20	9.24	21.0
	2.50	2.50	2.50	8.96	25.0
	2.50	2.60	2.60	8.89	26.5
	3.00	2.84	2.92	9.42	18.5

* The time in this experiment was 7 days; in all other experiments at this temperature it was 1 day.

natural marcasite when ground 1 h.† and heated at 300° in acid of 2.5 per cent saturated with hydrogen sulphide appeared to contain 30 per cent to 40 per cent pyrite, judged by the Stokes test. But further experiments showed that when marcasite was heated at 200° instead of 300°, or when the concentration of the acid was changed from 2.5 per cent to 2 per cent, a similar change in the marcasite took place. Thus under conditions (2 per cent H_2SO_4 at 200°) where pure or nearly pure synthetic marcasite was formed, natural marcasite appeared to change, judging from the Stokes test alone. No corresponding change in color was seen. Such products always flocculated decidedly, a behavior which is probably accountable

† Coarsely ground marcasite was unchanged when treated in this way.

for the results with the Stokes test.* When marcasite which had been subjected to the above treatment was heated in vacuo, it gave off no more gas than marcasite which had never been subjected to such treatment (Table III). The former, therefore, could hardly have contained occlusions which affected the Stokes test. Some change in the marcasite, probably some change in its surface, has doubtless taken place, but when all the facts are considered it seems impossible that there should be any change to pyrite. Equally puzzling is the irregular increase in pyrite from the highest acid concentrations; some unknown condition, perhaps the greater solvent power of strong acid, enables the difference in potential between the two forms to assert itself.

(d) *The contemporaneous precipitation of pyrite and marcasite.*—The simplest explanation one can offer for the relation found between the acidity and the percentage of marcasite in the synthetic disulphides formed from acid solutions, is that the pyrite and marcasite crystallize simultaneously. Our general knowledge of the subject of unstable forms is quite limited, but many cases are known where the unstable form appears first and is followed by a stabler form. In the case we are considering, the stable form is found in larger quantity in the products from low acid concentration and we know the acid increases with the progress of precipitation; the obvious inference is, therefore, that less pyrite is precipitated in the later stages of the process. It might be supposed that pyrite alone is precipitated until a certain limiting acid concentration is reached, when pure marcasite appears, but this hypothesis is easily disproved, for if the percentage of pyrite in any product is known, as well as the initial and final acid concentrations which prevailed during its formation, the limiting concentration can be easily calculated and yet a different calculated value is found for every product.

If precipitation occurred entirely at any given temperature, we could say without reserve that the percentage of marcasite in the product was a linear function of the acid concentration, at least within the errors of experiment, and then there would apparently be no escape from the conclusion that both crystalline forms of the disulphide come down together, the relative proportions at any temperature depending on the average acid concentration.

This conclusion cannot be hard and fast, however, because, owing to the considerable heat capacity of the bomb and its contents, several hours are required before the maximum temperature is reached, and consequently some of the product is precipitated while the temperature is rising (see fig. 2). It

* See p. 375 of this number.

was at first believed that the quantity of sulphide precipitated below the maximum temperature would decrease regularly with the increase in acidity, since the total quantity of product obtained at different temperatures diminished with the acid concentration. But experiment has shown that the relation is not so simple as that, and the question arises: Why are the final products at these maximum temperatures so simply

FIG 2.

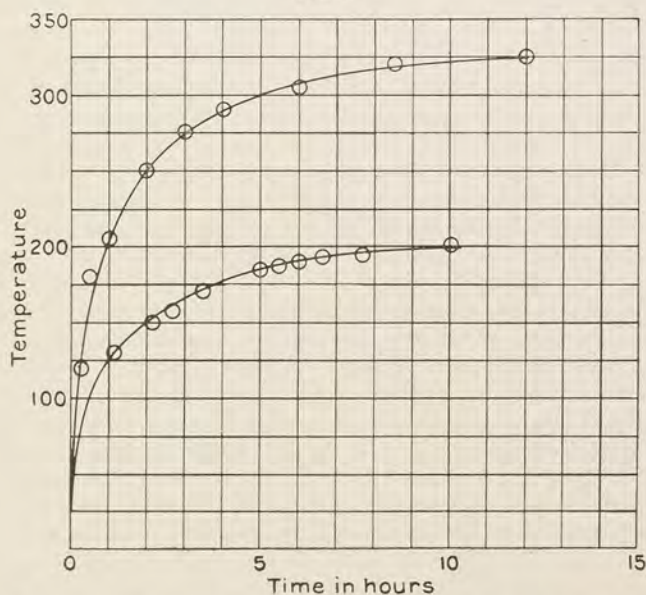


FIG. 2. Typical curves showing time required for a cold bomb to reach the temperature of the furnace.

related to the acidity? The most plausible explanation is that the influence of temperature is comparatively small in the interval in which precipitation occurs. We can get no adequate measure of this by comparing the curves for 200° and 300°, for experiment shows that when the furnace is set for 300° most of the product is precipitated (i. e., the hydrogen sulphide is nearly used up) by the time the maximum temperature is reached. Until we have more knowledge or can bring about precipitation at a constant temperature we can not state *quantitatively* the influence of either temperature or acidity. What we do know is the *direction* and *regularity* of both influences. It will be noticed in the figure (fig. 1) that the two lines representing the composition of sulphides from vari-

ous acids at 200° and 300° respectively, should intersect at an average acidity of about .05 per cent. For the reason given above, the only meaning which attaches to this is that in a furnace set for 300°, all the product would be precipitated when 200° was reached in an acid of this concentration.

The main conclusions in this paragraph are confirmed by the results obtained with hydrochloric acid solutions.

4. *Influence of hydrochloric acid.*—The influence of hydrochloric acid on the crystalline form of iron disulphide was regarded with much interest, not only because side reactions due to the oxidizing effect of sulphuric acid could thus be entirely avoided, but also because in this way any peculiar effect due to sulphuric acid could be eliminated and the specific influence of the hydrogen ion concentration could be put to test.

The same experimental methods were followed as before,—only ferrous chloride was substituted for ferrous sulphate. The ferrous chloride solution was prepared by partially dissolving a quantity of powdered iron in hot hydrochloric acid, pouring the mixture on to a filter, so that the excess of iron would keep the solution from oxidation, and catching the filtrate in a flask which was kept full of carbon dioxide by the passage of a continuous stream. After the excess of acid had been neutralized by sodium carbonate, the iron was determined and the solution then diluted with air-free water. The concentration actually taken in the experiments was equivalent to the ferrous sulphate solutions in previous experiments, and all the work was done at a maximum temperature of 300°. The products were better crystallized than any others.

TABLE V.

Showing the influence of hydrochloric acid in the formation of marcasite at 300°.

Initial acid in wt. %	Final acid in wt. %	Average acid in wt. %	($x - a$)	Percent pyrite
0.10	0.60	0.35	9.63	15.
.10	.82	.46	9.77	13.
.05	.69	.37	9.81	12.
.05	.25	.15	9.94	10.
.50	.90	.70	10.20	6.
.50	.90	.70	10.31	5.
.25	.93	.59	10.34	4.
.50	.86	.68	9.12	28.
.75	1.00	.88	9.13	28.

The numerical data are presented in Table V.* The first point to be noted here is that the range of acidity within which it is possible to work is very limited, for a comparatively low concentration, about 1 per cent, inhibits precipitation entirely. Such products as one can obtain within this range vary comparatively little in composition also. However, excepting in the highest concentrations, the percentage of pyrite is seen to diminish as the acid concentration increases. While the results are too limited in range to determine accurately the slope of the curve, it appears to be nearly the same as that for sulphuric acid solutions at 200°. The fact that any given quantity of hydrochloric acid exercises a greater specific influence on the crystalline form of iron disulphide than the chemically equivalent quantity of sulphuric acid may be explained by the greater hydrogen ion concentration in solutions of the former. Still, we should logically conclude also that the slope of the curve ought to be steeper from the same cause. This appears not to be true, but perhaps the numerical values are, as suggested above, too limited in range to make sure of it.

Hydrochloric acid solutions unquestionably give results which are analogous to sulphuric acid solutions in the following particulars: they give products containing marcasite which increases in quantity with increasing acid concentration; the highest acid concentrations give results abnormally high in pyrite; an acid concentration is found which inhibits precipitation entirely, and finally, the *product highest in marcasite is of the same composition as that highest in marcasite obtained from sulphuric acid solutions at 200° and 25°.*

G. *Synthetic marcasite.*—These facts lead to the suspicion that the above product may be pure marcasite. This suspicion is strengthened by the fact that acids of 0.6 per cent and 0.7 per cent average hydrochloric acid concentration give the same product. Measured by the Stokes constant for natural marcasite, the composition should be 95 per cent marcasite. We know that this constant varies somewhat in different natural specimens of marcasite, as well as pyrite, and that impurities affect it. The purest natural marcasite from Joplin, Missouri, contained no foreign metals, but it is possible it may have contained a little oxide of iron, which would certainly have raised the value of the constant. We have no positive evidence of this, but it is strange that under three different sets of conditions the same product should be obtained, unless that product were a chemical compound. There is another explana-

*It is interesting to note that with 0.05 per cent HCl solutions a precipitate of FeS_2 was obtained when no H_2S was introduced, due to the formation of H_2S by the interaction of sulphur and water at 300°. When the initial acid was greater the formation of H_2S in this way was not observed.

tion possible. The results in Table III do not prove that *very small quantities* of hydrogen sulphide might not be occluded by the products, and it may be that this apparent 5 per cent of pyrite is due to a slight occlusion, though there is no proof of it.

III. WURTZITE.

It has been shown in a previous paper* that crystalline zinc sulphide may be obtained by the action of hydrogen sulphide on acid solutions of zinc salts at sufficiently high temperatures. Nearly all our work was done on sulphate solutions, since chloride solutions for some unknown reason gave no crystalline products. Many of the products contained both the stable form sphalerite and the unstable form wurtzite,† and the experiments indicated that the more acid was the solution for any given temperature, the greater was the proportion of wurtzite; and the higher the temperature for any given acidity, the greater was the proportion of sphalerite.

It was hoped that a more thorough investigation would not only establish these points, but would also decide whether temperature and acidity were the sole determining influences on the crystalline form or whether other conditions, such as the pressure of the hydrogen sulphide, the time and the concentration of the zinc salt had any effect.

A. *Method for preparing wurtzite.*—Zinc sulphide is very difficult to crystallize—a fact which complicates the process of its formation and makes the conditions difficult to study. First, it needs a higher temperature than marcasite, not less than 250°, and secondly, it must be precipitated slowly; consequently a *double* tube was required in its preparation, for when an acidified solution of a zinc salt was saturated with hydrogen sulphide and heated in a *single* tube at 300°, only an amorphous precipitate was obtained. The procedure in our experiments was as follows: 20 cc of a solution containing measured quantities of zinc sulphate and sulphuric acid were dropped into a platinum tube 1.5 cm in diameter and 25 cm long, closed at the lower end. This was supported by a piece of glass tubing of convenient size, inside a larger glass tube 1.8 cm inside diameter also closed at the lower end. The outside tube, which contained a solution (either sodium thiosulphate or ammonium thiocyanate) yielding hydrogen sulphide when heated, was then sealed, enclosed in a steel bomb with water and heated to the desired temperature. After heating for the necessary time

* Allen, Crenshaw and Merwin, this Journal (4), xxxiv, 341, 1912; Zs. anorg. Chem., lxxix, 125, 1912.

† Sphalerite undergoes a reversible transformation into wurtzite at about 1020°; wurtzite is therefore unstable at lower temperatures.

the bomb was removed from the furnace and allowed to cool. The glass tube was removed and opened, the volume of solution remaining in the platinum tube was measured, the zinc sulphide filtered off and the final acidity determined as described in the chapter on marcasite. When sulphur was found mixed with the sulphide, it was removed by carbon disulphide before microscopic examination.

The wurtzite from these solutions never appeared in distinct crystals, but in radial parallel or felty aggregates of minute prisms. The sphalerite formed clear faceted crystals which were usually grouped, but rarely in single elongated dodecahedra. Regular groups usually appeared at first sight to be single, deeply cross-striated, hexagonal prisms up to 0.2^{mm} long, but further study indicated that they were strings of dodecahedra twinned after the spinel law. Some regularly branching groups were observed, made up of such prismatic forms all pointing outward.

Since sulphuric acid, even when dilute, is reduced by hydrogen sulphide at the temperatures of these experiments, an effort was made to use solutions of zinc chloride, acidified with hydrochloric acid. Although many experiments were tried at temperatures as high as 350°, crystalline zinc sulphide was never obtained from chloride solutions.

The necessity of using a double tube and sulphate solutions made it impossible to determine accurately the acid concentration at the time the zinc sulphide was being precipitated; the sulphuric acid was not only reduced by hydrogen sulphide but also distilled in considerable quantity from the inside to the outside tube. It was of course possible, however, to determine with accuracy the acid which remained at the end of the experiments, and this *final* acid concentration proved to be the factor which determined the crystalline forms of the products at any given temperature.

Although a discussion of the distillation and reduction of sulphuric acid is somewhat of a digression from the main purpose of this paper, it is introduced because it was a necessary part of the work and the results obtained are of considerable chemical interest.

B. Reduction of dilute sulphuric acid by hydrogen sulphide.—The reduction of dilute sulphuric acid by hydrogen sulphide was proven by the universal occurrence of sulphur in the products, and the formation of sulphur dioxide in many cases. This sulphur might be regarded as the product of a secondary reaction of sulphuric acid on sodium thiosulphate when that reagent was used, but it also appeared where ammonium thiocyanate was substituted for the thiosulphate, as well as where the sulphuric acid solutions were heated *directly*

with hydrogen sulphide.* Solutions which contained at the start 2 per cent of sulphuric acid were always partially reduced to sulphur after being heated to 300° for one day, while solutions which contained from 5 per cent to 10 per cent sulphuric acid were further changed to sulphur dioxide under similar conditions.

C. *Distillation of dilute sulphuric acid.*—The acidity of the solutions was still more seriously affected by the distillation of acid from the inside to the outside tube. The results of

TABLE VI.
Showing the distillation of dilute sulphuric acid at 300°.

Inside tube					Outside tube			
H ₂ SO ₄ taken	H ₂ SO ₄ from ZnSO ₄	Total H ₂ SO ₄	H ₂ SO ₄ found	Loss from inside tube	H ₂ SO ₄ taken (to decompose NH ₄ CNS)	H ₂ SO ₄ found	Gain in outside tube	H ₂ SO ₄ decomposed by H ₂ S
2.061 g.	0.136 g.	2.197 g.	1.599 g.	0.598 g.	0.677 g.	1.199 g.	0.522 g.	0.076 g.
1.603	none	1.603	1.140	0.463	0.677	0.940	0.263	0.200
2.061	0.118	2.179	1.516	0.663	0.677	1.086	0.409	0.254

Table VI will make this plain. The quantities of acid taken (Columns 1 and 6) were determined by measuring out the required volume of acid of known strength. The zinc being practically all precipitated, in the experiments quoted, its equivalent in sulphuric acid is added to 1 (Column 2) to give the total acid taken in the inside tube (Column 3). The acid left in the inside platinum tube was determined by titration of the filtrate from zinc sulphide. It should be stated here that it was ascertained by blank experiment that no sulphuric acid was formed from the thiocyanate in the outside tube. The amount of sulphuric acid in Column 7 was determined by precipitation with barium chloride. A comparison of the results in Column 7, with determinations of the free acid by direct titration, showed that the latter were always lower because presumably the acid had been partly neutralized by the bases in the glass, which is always considerably attacked under these conditions (300°). The figures in the last column refer to the differences between the losses from the inside tube and the gains in the outside tube. Some of the acid, as we have already learned, is reduced to sulphur and sulphurous acid, a fact which accounts for this.

* See p. 396.

The loss of sulphuric acid from the inside to the outside tube by distillation was found to be fairly constant, other conditions remaining unchanged. Fig. 3 shows that the relation

FIG. 3.

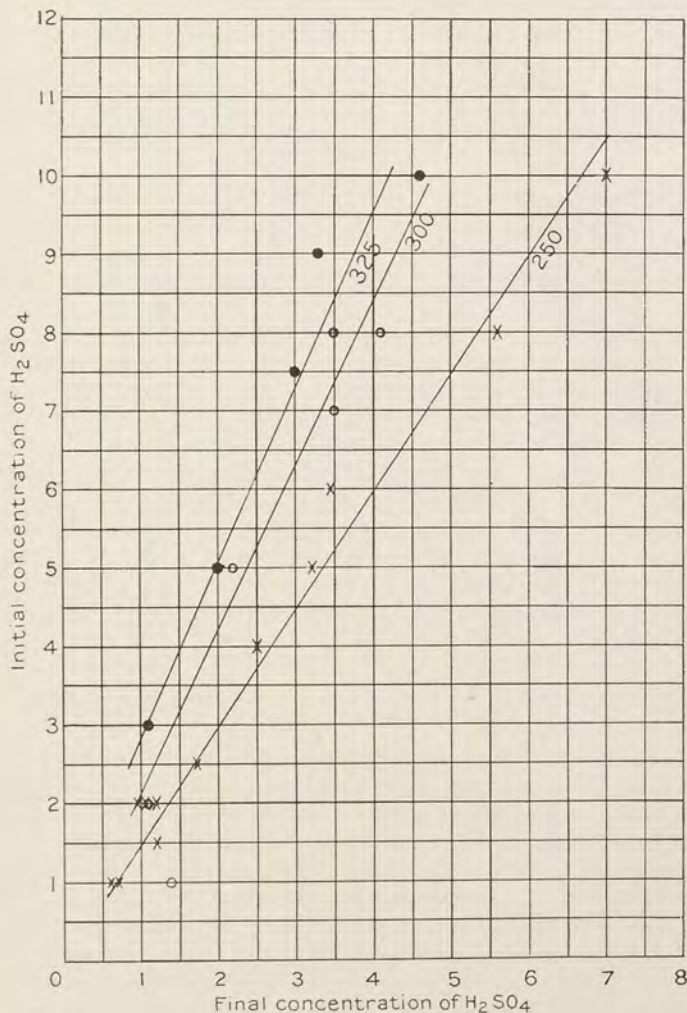


FIG. 3. Showing the relation of the initial to the final acid concentration.

between the initial and the final acid concentration is approximately linear. Since it appears from what follows that the final acid concentration is the factor which determines the

crystal form of the zinc sulphide at any given temperature, we found this plot useful in ascertaining what initial concentration to choose for any desired final concentration.

D. *The precipitation which takes place before the tube reaches its final temperature.*—In the case of dilute acids it was impossible to prevent some precipitation of zinc sulphide during the time required for heating the tubes to the desired temperatures, but this was reduced to a minimum by having the furnaces heated to the necessary temperature before the bombs were introduced. The time required for the bomb to reach the temperature of the furnace is graphically shown in fig. 2.

A very small amount of precipitate was formed below 250° since below this temperature H_2S is not formed very rapidly from the reagents in the outside tube. It is also true that *zinc sulphide precipitated below 250° is amorphous* and easily recognized by the microscope. In experiments done at 250° , therefore, the time required for heating the bomb may be disregarded since we are concerned only with the crystalline portion of the product. At 300° and 325° however, when the acid concentration is low, a considerable amount of zinc sulphide is precipitated between 250° and the final temperature, and we should therefore find relatively too much wurtzite in the products, since with falling temperature and constant acidity the proportion of this crystalline form increases (see pp. 421–426). Experimental evidence confirms this (see p. 420). If the initial acid concentration is fairly high (over 3 per cent) practically no precipitation occurs before the maximum temperature is reached.

E. THE EFFECT OF CHANGING CONDITIONS OTHER THAN ACID CONCENTRATION.

1. *Hydrogen Sulphide pressure.*—Before the above serious variation to which the very important condition—acid concentration—was subjected, was fully realized, some efforts were made to control the pressure of hydrogen sulphide. This was done by varying the quantity of reagent, either sodium thiosulphate* or ammonium thiocyanate,† which yields the hydrogen sulphide. It proved to be a physical impossibility to vary the pressure greatly without varying the acid concentration greatly; to judge from the pressure manifested when the tubes were opened, it varied a number of atmospheres, but in these experiments there was found no appreciable influence on the crystalline form which could not be directly ascribed to the acid concentration.

* Allen, Crenshaw and Johnston, loc. cit., p. 186.

† Weinschenk, Zs. Kryst., xvii, 495, 1890.

2. *Zinc concentration.*—The experiments which were made on this point were all carried out at 300° and lasted 24 hours. The products from the more concentrated zinc solutions usually contained considerable amorphous material while the crystalline portion was generally poorly developed. The microscopic analyses are therefore more difficult and presumably less trustworthy. Nevertheless the study of the analyses of products

TABLE VII.

Influence of zinc concentration on the crystal form of zinc sulphide at 300°. Time 24 hours.

Initial H_2SO_4 in wt. %	Final H_2SO_4 in wt. %	$\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ in wt. %	Percent amorphous	Per cent wurtzite in crystal- line portion	Per cent wurtzite in products from 2% $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ solutions and the same final H_2SO_4 .
2	2.0	5	50	0	40
2	2.9	5	25	65	90
2	1.6	5	5-10	5	15
2	1.5	5	40	15-20	10
2	2.5	10	?	50	70
2	3.7	10	?	50	100
2	2.7	10	considerable	50-75	70
2	3.0	15	50	100	100
2	3.1	15	25	100	100
2	5.6	15	5-10	0	100
2	8.0	20	25	100	100
2	6.7	20	35	100	100
2	6.7	20	25	100	100
2	2.9	20	90	50	100

precipitated from solutions containing 5 per cent to 20 per cent of hydrous zinc sulphate (Table VII) brings out a number of interesting points. First, an increase in the zinc concentration increases the percentage of wurtzite in the product, as is shown by a comparison of the results in Table VII, with the product obtained from the same initial acid (2 per cent) and a *dilute* zinc sulphate solution (2 per cent) (Table XI). In the latter, indeed, *only sphalerite* was obtained. The observer might at first attribute this effect to the influence of the varying zinc concentration. There is a simpler explanation, however. The action of hydrogen sulphide on the zinc salts results in the *formation of sulphuric acid* as well as zinc sulphide, and, since the sulphide precipitate naturally increases with the zinc concentration, so also does the *acidity* increase.

If we compare products obtained from the same final acid, the initial zinc concentration varying in one series and remaining constant (2 per cent) in the other (Tables VII and XI), we shall find that more than half the results agree within the limits of error of the microscopic determination. In other cases the quantity of sphalerite obtained from concentrated zinc solutions is greater than from dilute zinc solutions. This variation, however, may be explained if we note that in one series of experiments the acid concentration is rising, in the other falling (see pp. 421).

3. *Sodium Sulphate*.—In the earlier stages of our work in order to prevent the distillation of sulphuric acid from the platinum tubes (see p. 414) sodium sulphate was introduced to lower the vapor pressure. By this means it was possible to keep the acid concentration much more nearly constant during the course of the precipitation of the zinc sulphide, but the products were usually not well crystallized and in many cases

TABLE VIII.

Influence of Na₂SO₄ on the crystalline form of ZnS at 300°.

Initial H ₂ SO ₄ in wt. %	Final H ₂ SO ₄ in wt. %	Na ₂ SO ₄ grams	Time	% Amorphous	Crystalline	
					% Wurtzite	% Sphalerite
2	2.2	1.0	1 day	60-75	50	50
2	1.9	2.0	2	nearly all	?	?
2	2.1	2.0	1	100	----	----
5	3.4	1.0	1	20	?	nearly all
5	3.5	2.0	1 $\frac{3}{4}$	25	67	33
5	4.0	5.0	1	50	50	50
8	6.2	2.0	1	some	?	some
10	6.8	2.0	1 $\frac{3}{4}$	15	?	100
10	7.0	2.0	1	----	no ZnS	----
10	6.6	5.0	1	40-50	100	?
10	7.6	5.0	1	25	100	0
10	7.5	5.0	1	5	70-80	20-30
15	10.2	5.0	1	20-30	90-95	5-10
15	11.4	5.0	1	30-40	90-95	5-10
20	12.1	5.0	1 $\frac{3}{4}$	0	99	<1

an estimate of the percentage of wurtzite could not be made. The results are shown in Table VIII. Almost without exception the products show more sphalerite than those obtained from solutions of the same *final* acid concentration where sodium sulphate was not used. Although this may be due specifically to the presence of sodium sulphate it seems more probable that the variation is due to the reduction of the

hydrogen ion concentration owing to the formation of sodium acid sulphate. This hypothesis seems to be supported by the fact that the precipitates from 2 per cent initial sulphuric acid solutions were largely amorphous when sodium sulphate was used, whereas when it was not used the products from 2 per cent sulphuric acid were well crystallized, becoming amorphous only when the acid concentration was reduced to less than 1 per cent.

4. *Time*.—Since wurtzite is unstable below 1020° * it was thought that a longer heating of the products with the solution out of which they crystallized would cause the wurtzite to change into sphalerite. It was impossible to obtain conclusive evidence on this point owing to the fact that *the time could not be increased without a corresponding decrease in acid concentration* due to the reduction of the sulphuric acid by the hydrogen sulphide, which had to be renewed continually to prevent solution of the zinc sulphide. The duration of each experiment is given in the tables (X-XII) and it will be seen that at 250° (Table X) (the reduction of the acid is slow enough to allow a long heating at this temperature) there is no increase in sphalerite in the products when they are heated 5 days instead of 3 days, provided the acid concentration does not fall below a certain limit. The following experiment shows that at 325° wurtzite is not changed to sphalerite in one day if the acid concentration is high but considerable change occurs in one day if the acid concentration is low.

F. *Evidence that wurtzite is changed to sphalerite by heating with dilute acid*.—A product which had been made from a solution, the final acidity of which was 4.2 per cent, by heating for one day at 325° , consisted entirely of wurtzite. This wurtzite was again put into a platinum tube with 3 per cent sulphuric acid saturated with hydrogen sulphide and sealed in a glass tube containing 0.5 g. ammonium thiocyanate and 0.66 g. sulphuric acid dissolved in 15 cc of water in the outside tube. The air in the glass tube was replaced by hydrogen sulphide before sealing. Except for the acid concentration this tube was similar to the one in which the wurtzite had been formed. After heating for one day microscopic examinations showed that the wurtzite had well-formed new crystals of sphalerite growing on it. The acid concentration had fallen to 1.45 per cent owing to distillation and reduction.

Additional evidence on this point is given in Table IX. As has been stated (page 416), some zinc sulphide is precipitated from solutions having an initial acid concentration of 3 per cent or less before the tubes reach the temperature of the furnace. When the furnaces were set for 300° , or higher

* Allen, Crenshaw and Merwin, loc. cit.

TABLE IX.

Showing that wurtzite is changed to sphalerite by heating with dilute acid.

Time in hours	Temperature of furnace	Initial H ₂ SO ₄ in wt. %	Final H ₂ SO ₄ in wt. %	Product		
				Composition of Crystalline Part		% Amorphous
				% wurtzite	% sphalerite	
7	300°	2.0	1.9	100	0	trace
8	300°	3.0	2.2	0	100	5-10
7	300°	3.0	2.5	95	5	1-2
8½	325°	3.0	1.9	95	5	2-3
11	300°	2.0	1.1	33	67	trace
12	300°	3.0	2.0	60	40	2-3
11	300°	3.0	2.4	100	0	5-10
12	325°	3.0	1.7	10	90	5-10
24	300°	2.0	1.5	0	100	5-10
24	300°	3.0	2.0	0	100	5
24	300°	3.0	1.9	50	50	0
25	325°	3.0	1.1	0	100	trace

temperatures, much of this first precipitate was crystalline and contained a larger percentage of wurtzite than that portion which was precipitated after the final temperature was reached. The products which were obtained (Table IX) at the end of 7 or 8 hours must have been precipitated before the temperature of the furnace (column 2) was reached. With one* exception they consist largely of wurtzite.

At the end of 11 or 12 hours the percentage of wurtzite is, in general, much less. This is, no doubt, partly due to the fact that more zinc sulphide has been precipitated and this must have been largely sphalerite since it was precipitated after the maximum temperature had been reached. In every case except one, however, the wurtzite had entirely disappeared at the end of 24 hours. It is evident that the wurtzite present at the end of 8 and 12 hours has been changed to sphalerite by further heating with dilute acid.† This cannot be explained as a simple case of an unstable form precipitat-

* We have no explanation for this apparent exception. We have found that the time at which precipitation begins varies considerably in different experiments, and it may be that in this case no precipitation took place until the temperature of the furnace was practically reached.

† It might be objected that the more soluble wurtzite had been dissolved away in these cases, leaving the sphalerite. This could not have occurred since an excess of hydrogen sulphide was always found at the end of the experiments and the weight of the products was always *greater* at the end of 24 hours. The wurtzite had evidently been transformed and probably by solution and recrystallization, since there is no evidence that the change occurred in the solid state.

ing first and changing to the stable form with time, since it is specifically dependent on the acid concentration. In Table XI, it is shown that at 300° even after 48 hours wurtzite is entirely unchanged provided the acid concentration is kept sufficiently high. The evidence given above forces the conclusion that *the crystal form of zinc sulphide*, under the conditions of our experiments, depends on the *final concentration* of acid with which it is heated, and not on the concentration out of which it is precipitated. For this reason the final acid concentration has been used in plotting the results.

The above conclusion is valid *only when the concentration of the acid falls* during an experiment, and this always occurred when 2 per cent zinc sulphate was used. This concentration of zinc sulphate yielded the best developed crystals and was always used except in the series where the influence of the zinc concentration was studied. If the acid increases during an experiment and the initial acid concentration is low enough for the formation of sphalerite, this sphalerite will naturally persist, since it is the stable form, after the acid has increased to the concentration from which wurtzite will form. In such a case the crystalline form depends on the acidity at the time of formation. In the concentrated zinc solutions, Table VII, the acid increased during the experiments, and this accounts for the fact that more sphalerite was found there in some cases than in products from dilute zinc solutions (2 per cent) with the same final acid concentration.

G. *The influence of acidity in the formation of wurtzite.*—The evidence accumulated by a more complete study of this subject entirely corroborated the earlier indications. It has been shown that, in all probability, the changing of other conditions, such as the pressure of the hydrogen sulphide, the zinc concentration, and the addition of sodium sulphate has no appreciable effect on the crystalline form. The influence of acid, however, is in some ways even more striking than it was in the case of marcasite. At 300° and 325° we were able to obtain crystalline products varying in composition from pure sphalerite, through mixtures of the two forms, to pure wurtzite. In the iron disulphide mixtures, we were not able to obtain from acid solutions a product which contained more than about 50 per cent of the stable form (pyrite).

In the investigation of the two sulphides of zinc, however, many difficulties were encountered which were not met with in the case of the disulphides of iron. In the first place the range of temperature was very restricted. As has been said, only amorphous zinc sulphide was obtained below 250° , and, as is shown in Table XIII, only sphalerite was obtained at 350° or higher, though the acid concentration was increased to the point at which no precipitation took place.

FIG. 4.

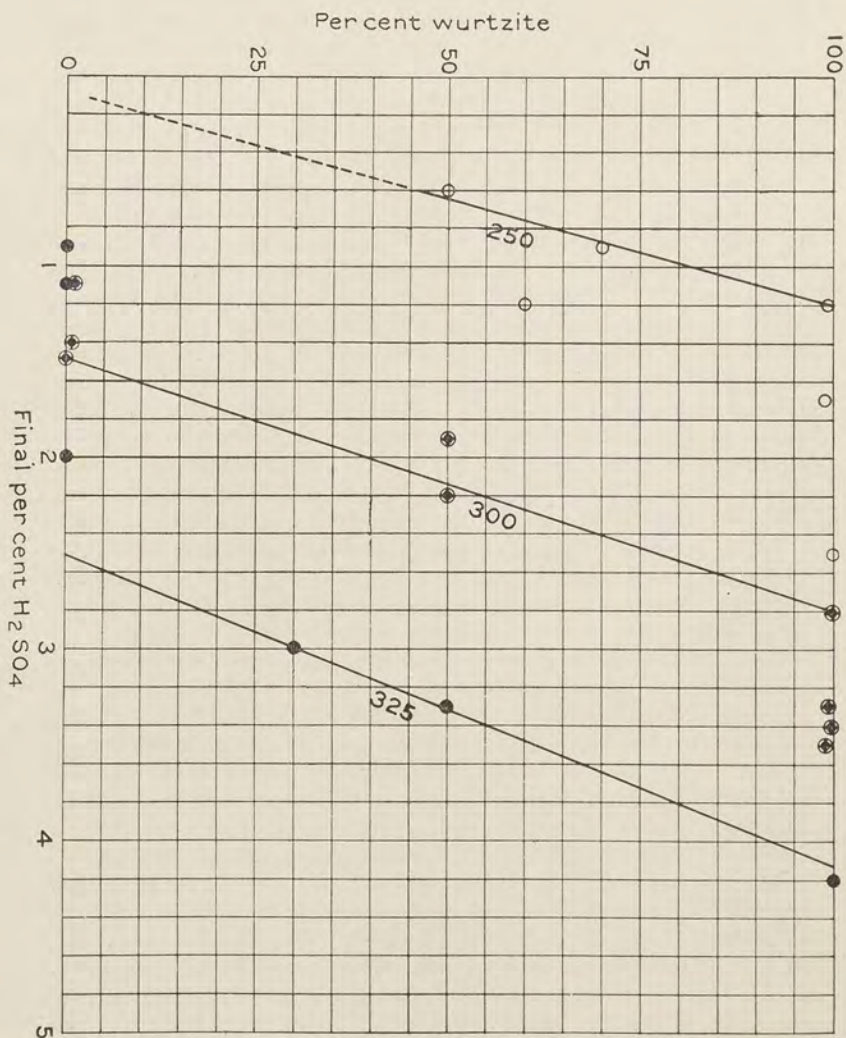


FIG. 4. Showing influence of acid concentration on the crystalline form of zinc sulphide at 250°, 300° and 325°. O = 250°; ⊕ = 300°; ● = 325°.

The determination of the percentage of wurtzite in the products was done by microscopic estimation, and naturally the accuracy of this method, especially as the wurtzite was usually coated with sphalerite and frequently mixed with amorphous material, can not be compared to that of the Stokes reaction which was used with the disulphides of iron. When the products consisted entirely of one of the two forms, the microscopic estimate was, of course, entirely satisfactory.

The results are given in Tables X to XII, and plotted in fig. 4. The final acid concentrations, instead of the average concentrations, are here taken as abscissas for reasons already given (p. 421).

1. *The question of a linear relation between the percentage of wurtzite and the final acid concentration.*—Considering the difficulties of the work the results show surprising regularity. When the determinations were made, the microscopist was without knowledge of the experimental conditions under which the different products were formed and the estimates could not have been biased in any way. The results are of more interest, because of the similarity to those obtained in the synthesis of pyrite and marcasite. The reader will bear in mind that in the latter case a linear relation was found between the acidity and the percentage of marcasite, and that the only satisfactory explanation of this relation was that the two crystalline forms were precipitated at the same time, the proportions varying with the acidity. There are some facts about the formation of the zinc sulphides which are not in accord with the supposition of the simultaneous precipitation of the two. The wurtzite is very commonly coated over with sphalerite, which must, of course, have formed later. There are, however, often separate crystals of sphalerite which may have been formed simultaneously with the wurtzite and before the final coating. Simultaneous precipitation of the two forms is, perhaps, in this case, not a necessary consequence of a linear relation between acidity and composition, for the reason that synthetic wurtzite appears to undergo change into sphalerite subsequent to its formation whenever the acidity falls sufficiently, while marcasite never suffers a similar change so far as we know. Still, in view of the difficulties both in following the experimental processes and in estimating the composition of the products, it would be unwise to insist on the existence of a linear relation here, though the parallelism between the results on the synthesis of the zinc sulphides and those on the iron disulphides is remarkable. The results, however, leave no doubt of the specific influence of acid on the crystalline form of zinc sulphide, nor of the conclusion that when wurtzite and sphalerite are formed together, the products precipitated

TABLE X.

Influence of acid on the crystalline form of ZnS at 250°. All solutions contained 2% ZnSO₄·7H₂O and were precipitated by H₂S from 0.5 g. NH₄CNS.

Initial H ₂ SO ₄ in wt. %	Final H ₂ SO ₄ in wt. %	Time	Product		% Amorphous
			Composition of Crystalline Part		
			% wurtzite	% sphalerite	
1.0	0.6	3 days	50	50	60
1.0	0.7	4 "	?	?	80
1.5	1.2	3 "	60	40	50
2.0	0.9	4 "	70	30	15
2.0	1.1	3 "	5	95	5
2.0	1.2	5 "	99	1	0
2.5	1.7	5 "	99	1	5
4.0	2.5	2 "	100	0	0
5.0	---†	2 "	100	0	5
6.0	2.9	3 "	no precipitate of ZnS		
8.0	5.6	3 "	"	"	"
10.0	7.0	2 "	"	"	"

TABLE XI.

Influence of acid on the crystalline form of ZnS at 300°. All solutions contained 2% ZnSO₄·7H₂O and were precipitated by H₂S from 0.5 g. NH₄CNS.

Initial H ₂ SO ₄ in wt. %	Final H ₂ SO ₄ in wt. %	Time	Product		% Amorphous
			Composition of Crystalline Part		
			% wurtzite	% sphalerite	
0	0.3	2½ days	----	----	100
1.0	1.4	3 "	2*	98	75
1.0	-----†	4 "	0	100	5
2.0	-----†	-----	0	100	0
2.0	1.1	2 "	2 or 3	97-98	5
2.0	1.5	1 "	0	100	10
3.0	1.9	1 "	50	50	0
5.0	2.2	1½ "	50	50	0
8.0	3.5	1½ "	99	1	0
8.0	2.8	1 "	100	0	0
8.0	3.7	1 "	75	25	0
10.0	3.4	2 "	100	0	0
10.0	3.3	2 "	100	0	0
10.0	3.7	1 "	25	75	0

* This wurtzite consisted of only 2 or 3 minute pieces of detached crusts.

† Not determined.

TABLE XII.

Influence of acid on the crystalline form of ZnS at 325° . All solutions contained 2% $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ and were precipitated by H_2S from 0.5 g. NH_4CNS .

Initial H ₂ SO ₄ in wt. %	Final H ₂ SO ₄ in wt. %	Time	Product		% Amorphous
			Composition of Crystalline Part		
			% wurtzite	% sphalerite	
3.0	0.9	1 day	0	100	15
3.0	1.1	1 “	0	100	trace
5.0	2.0	1 “	0	100	0
6.0	2.3	1 “	60	40	0
7.5	3.0	1 “	30	70	0
9.0	3.3	2 “	50	50	0
9.0	4.2	1 “	100	0	0
10.0	4.6	1 “	no precipitate of ZnS		

from higher acid concentrations contain higher percentages of wurtzite.

2. *Conditions necessary for the genesis of either form of zinc sulphide alone.*—Conclusions drawn from experiments which resulted in products consisting entirely of wurtzite or entirely of sphalerite were much more satisfactory, since the microscopic analyses of such products were naturally more certain. At three of the temperatures investigated, 250° , 300° and 325° , it was found that when the final acid concentration remained above a certain definite limit, wurtzite* was the only crystalline form obtained. At two of the temperatures (300° and 325°) a final acid concentration was determined below which sphalerite* was the only crystalline form obtained. When the final acid concentration lay between these limits, both wurtzite and sphalerite were found in the products.

At 250° (Table X) practically pure wurtzite was obtained whenever the final acid remained as high as 1.2 per cent; if the acidity fell to 0.6 per cent the percentage of wurtzite was reduced to 50 per cent, but further reduction in the quantity of wurtzite was impossible since weaker acids gave only an amorphous product. It seems certain that if a crystalline product could be obtained, a concentration of less than 0.5 per cent sulphuric acid would be necessary for the formation of pure sphalerite at this temperature.

At 300° (Table XI) it was possible to determine the final acid concentrations necessary for the formation of either crystalline form alone. Practically pure sphalerite was obtained

* Amorphous zinc sulphide was sometimes admixed.

in every case when the final acidity was not higher than 1.5 per cent; pure wurtzite resulted when the final acidity was 2.8 per cent or higher.

At 325° (Table XII) pure sphalerite was obtained from final acids of 2 per cent concentration or less; pure wurtzite was not obtained until the final acid rose to 4.2 per cent.

At 350° (Table XIII) sphalerite only was obtained in every experiment. At this temperature the necessary acid concentra-

TABLE XIII.

Influence of acid on crystalline form of ZnS at 350°. All solutions contained 2% $\text{ZnSO}_4 \cdot 7\text{SH}_2\text{O}$ and are precipitated by H_2S from 0.5 g. NH_4CnS .

Initial H_2SO_4 in wt. %	Final H_2SO_4 in wt. %	Time	Product
1	0.4	1 day	Some sphalerite, much amorphous, no wurtzite
5	4.2	1 "	All sphalerite
10	5.1	1 "	Probably all sphalerite
10	4.3	1 "	All sphalerite
10	4.2	1 "	Some sphalerite, much amorphous, no wurtzite
12	4.4	1 "	No precipitate
15	5.9	1 "	" "

tion for the formation of any wurtzite at all must be higher than 5.1 per cent, above which no precipitate was obtained.

It is evident from these experiments that the higher the temperature the higher the acid concentration necessary to condition the formation of the unstable form, wurtzite, alone. The same was found to hold true for marcasite.

In fig. 5 are plotted the final acid concentrations necessary for the formation of either form of zinc sulphide alone, against the temperature. Conditions of temperature and acidity represented by the area above the line AB give rise to pure wurtzite. The area below the line CD represents the conditions for the formation of pure sphalerite, while in the area between the two lines mixtures will occur. From this plot the acid concentration necessary for the formation of wurtzite at any given temperature may be determined. It is unfortunately thus far impossible to obtain crystalline zinc sulphide at ordinary temperature, and so great an extrapolation of the curve AB would be unconvincing, but the indications are that only a very slight acidity would be necessary for the formation of pure wurtzite, if the rate of formation could be so controlled as to give a crystalline product at ordinary temperatures.

IV. NATURAL GENESIS OF THE SULPHIDES OF IRON AND ZINC.

In the beginning of this paper, it was stated that former experiments of the authors showed that only the stable forms of the sulphides of iron (FeS_2), zinc (ZnS), and mercury (HgS), viz: pyrite, sphalerite, and cinnabar, could be obtained from alkaline solutions, and the corresponding unstable forms, marcasite, wurtzite and meta-cinnabar (?) had only been

FIG. 5.

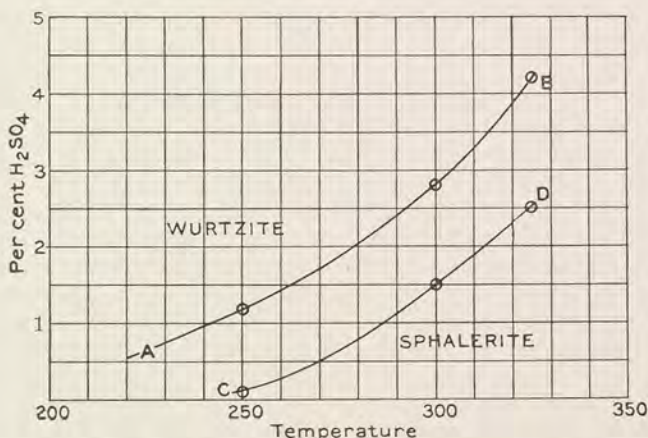


FIG. 5. Fields of precipitation of sphalerite and wurtzite.

obtained from acid solutions. A revision of a portion of that work in the present paper confirms the former results. Some new evidence bearing on the genesis of several of these minerals in nature has recently been brought to our attention. Our experiments on the formation of pyrite from alkaline solutions extended from 300° down to 70° . Pyrite had also been observed as a product of alkaline waters in nature at a temperature of 55° .* Evidence is now at hand which proves that from *cold alkaline solutions* also, pyrite and not marcasite is obtained.

A. *Pyrite from cold alkaline solutions.*—Mr. C. E. Sieben-thal,† of the U. S. Geological Survey, has made observations on a number of springs in which it can hardly be doubted that pyrite is now forming. These are the “White Sulphur” and “Black Sulphur” occurring in the town of Sulphur Springs, Arkansas. Both contain a dark sediment which has separated

* In the Carlsbad Springs. See Daubrée, *Géologie expérimentale*, p. 93 (Paris, 1879).

† Bull. U. S. Geol. Survey 606, Origin of the Joplin Lead and Zinc Deposits. In preparation.

from the water and which has been shown by analysis to consist largely of ferrous sulphide mixed with much smaller quantities of the sulphides of zinc, lead and copper. Cementing together the sand grains of both springs was also found *pyrite* in microscopic crystals, on many of which Merwin was able to identify the cube and octahedron. *No marcasite was found.* The waters of these springs closely resemble that of deep wells in the same geological horizon; they are predominantly alkali chloride and carbonate waters, they smell of hydrogen sulphide and are faintly alkaline.* Thus it becomes evident that the alkaline nature of the water irrespective of the temperature is sufficient to condition the formation of pyrite. Mr. Siebenthal has kindly placed at our disposal two samples of sediment from deep wells which further correlate natural processes with those of the laboratory. One of these wells is in St. Louis, Missouri, the other in Columbus, Kansas. The waters from both wells are of the same general character as the springs; they are not only decidedly alkaline, but contain a recognizable excess of soluble sulphide. The mud was deposited or settled after the waters had been pumped into storage reservoirs and had stood for an unknown time, probably about a year.† The sludge consisted of ferrous sulphide, free sulphur, which was dissolved out by carbon disulphide, and a substance having the color of ground pyrite, insoluble in hydrochloric acid, giving tests for both iron and sulphur, and showing no crystal form when examined under the microscope. In addition to these products the sediment from the Kansas well contained also a crystalline substance resembling pyrite but in crystals too small for identification.‡ Now, we know that a soluble polysulphide gives with a ferrous salt a precipitate of ferrous sulphide and sulphur, and we have observed in the laboratory that they unite at 100° to form amorphous disulphide, which in time crystallizes to pyrite. In the waters of the springs and wells which we have just cited, it is plain that the same processes go on very slowly at ordinary temperature.

B. *Paragenesis of marcasite and wurtzite with calcite.*—We have stated previously that marcasite is commonly a product of surface waters and have concluded that it may have formed from acid solutions, because the solutions from which it crystallizes are doubtless formed in many cases by the oxidation

*Both are alkaline toward rosolic acid and the White Sulphur water gives a trace of color with phenolphthalein. Small recent calcite crystals and recent quartz crystals occur in the Black Sulphur Spring.

†Mr. Siebenthal's investigations have brought out the fact that these are not unusual cases, but that the deep wells of this region in practically all cases yield a sediment of similar nature.

‡It was impossible to use the Stokes method to identify this substance, for not only was the quantity at our disposal too small but it was mixed with vegetable matter which could not be removed.

of sulphides, including pyrite or marcasite. Mr. Siebenthal has recently submitted some specimens of marcasite imbedded in calcite from Crystal Cave, Joplin, Missouri; and Mr. J. B. Umpleby a specimen of wurtzite also imbedded in calcite. The nature of these crystals indicates that they did not develop in free space, but that they crystallized simultaneously with calcite.* If so, the marcasite and wurtzite must have crystallized from solutions containing no stronger acid than carbonic acid, and probably at the ordinary temperature. It should be borne in mind that all the solutions used in our experiments, though dilute in some cases, were incontestably acid or incontestably alkaline, so that the specific influence of each is unquestionable. The nearest approach to the above conditions we have been able to employ are given on page 404, where we found that pure marcasite, or at any rate very nearly pure marcasite, was obtained from a solution containing 0.015 per cent sulphuric acid. Between this degree of acidity and very slight alkalinity† at ordinary temperatures, there exists a narrow field which has not been explored, nor does it present a promising field for exploration. We only know that in solutions containing only hydrogen sulphide, and therefore close to neutrality (reaction with ferric hydroxide suspended in water), pyrite is obtained at 150°.‡

We have also shown that wurtzite, in the temperature interval where it could be crystallized, was formed from acid solutions, and the concentration of the acid demanded for the inhibition of sphalerite grows less with descending temperature as it does with pyrite.

C. *Paragenesis of pyrite with calcite.*—Pyrite also may be contemporaneous with calcite. A specimen of both marcasite and pyrite in calcite was obtained by Mr. Siebenthal and examined by Dr. Merwin.§ The latter believes that we have here two distinct generations of iron disulphide, the marcasite before the pyrite, and each contemporaneous with calcite. It would be unwise to attempt a discussion of the problem here presented without further evidence, but it might be suggested that calcite has been formed in the laboratory by precipitation with alkali carbonate, as well as from carbonic acid solutions, and its occurrence in recent crystals in the slightly alkaline waters of the sulphur springs above cited proves also that pyrite and calcite can form from the same solutions.

It is also possible that in some cases pyrite and marcasite form together in nature, though the specimen in question does not appear to have formed in that way. Our experiments

* H. E. Merwin, The simultaneous crystallization of calcite and certain sulphides of iron, copper and zinc, this Journal, (4), xxxviii, p. 355, 1914.

† The waters of the sulphur springs just cited were almost neutral.

‡ This Journal, (4), xxxiii, 181, 1912; Zs. anorg. Chem., lxxvi, 215, 1912.

§ Loc. cit.

show conditions of temperature and acidity under which the two minerals may be formed at will together and apparently simultaneously.

Summary.

1. Our former results on the genesis of marcasite and wurtzite have been reinvestigated, the former conclusions have been confirmed and new data determined. The specific influence of acidity and alkalinity on the crystalline form of the sulphides investigated has been much more rigorously demonstrated. Only from acid solutions were the unstable forms obtained. The sulphides were prepared by the action of hydrogen sulphide and sulphur on acidic solutions of zinc salts and by hydrogen sulphide and sulphur on acidic solutions of ferrous salts. The unstable forms were usually mixed with the corresponding stable forms, viz.: sphalerite and pyrite, and the composition of the mixtures was determined, approximately for the zinc sulphides, by microscopic estimation; and within 1 to 2 per cent by the Stokes method for the iron disulphides.

2. As previously found, the higher the maximum temperature of experiment, other conditions remaining unchanged, the greater the quantity of the stable form, pyrite or sphalerite, obtained in the product.

3. As previously concluded, the higher the percentage of acid in the solution, other conditions remaining unchanged, the greater in general the quantity of the unstable sulphide, marcasite or wurtzite. The relation between the percentage of marcasite and the average acidity was practically linear for maximum temperatures of 200° and 300°. There are also indications of a similar relation in the case of wurtzite. In the case of wurtzite, however, the final acid was found to be the determining factor, since at 300° and 325° wurtzite appears to change into sphalerite when heated with sufficiently dilute acid. The temperature-acid field in the case of zinc salts may be divided by two boundary curves into three sub-fields, a high acid field in which only wurtzite is obtained, a low acid field where only sphalerite is obtained, and an intermediate field where mixtures of the two are obtained.

4. No crystalline zinc sulphide could be obtained from hydrochloric acid solutions, but the iron disulphides were crystallized from them, and always contained much more marcasite for an equivalent quantity of acid; i. e., hydrochloric acid has a much greater influence on the crystalline form than an equivalent quantity of sulphuric acid, which should be the case if the hydrogen ion concentration were the real determining factor.

5. The acid concentration required to give rise to pure marcasite or pure wurtzite falls with the temperature and is close to neutrality for marcasite at ordinary temperature, and probably so for wurtzite.

6. Several conditions other than acidity and temperature were varied in the formation of wurtzite, where the process was necessarily more complicated; these were zinc concentration, addition of sodium sulphate to the solutions, and hydrogen sulphide pressure. None of these had any influence except as they affected the acidity.

7. At the temperatures of 25° and 200° from sulphuric acid solutions and at 300° from hydrochloric acid solutions, we obtained a product containing 95 per cent of marcasite as compared with the purest natural marcasite we have had in our hands. Since this determination depends on the quantity of iron dissolved from the mineral under definite conditions, and different natural specimens vary somewhat, it may be that this product is pure synthetic marcasite.

8. Some new data on the genesis of the natural minerals are cited.

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Carnegie Institution of Washington,
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